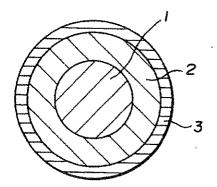
EXHIBIT G

Part 2

....

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FIG.1



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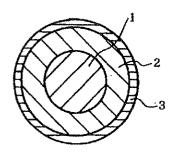
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(54) 【発明の名称】 スリーピースソリッドゴルフポール

(57)【要約】

【目的】 ソリッドゴルフボールの特徴である良好な飛び性能及び耐久性を劣化させることなく、フィーリング及びコントロール性を向上させ、トータルバランスに優れたソリッドゴルフボールを得る。

【構成】 センターコア1と、中間層2と、カバー3とからなるスリーピースソリッドゴルフボールとし、センターコア1を直径29mm以上、比重1、4未満、中間層2を厚さ1mm以上、比重1、2未満、JIS-C硬度85以上、カバー3を厚さ1~3mmに形成する。



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【特許請求の範囲】

【請求項1】 センターコアと、中間層と、カバーとからなるスリーピースソリッドゴルフボールにおいて、センターコアが直径29mm以上、比重1.4未満、中間層が厚さ1mm以上、比重1.2未満、JIS-C硬度85以上、カバーが厚さ1~3mmであり、かつ上記中間層の比重がセンターコアの比重よりも小さいことを特徴とするスリーピースソリッドゴルフボール。

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【請求項2】 中間層が高反発性アイオノマー樹脂を主 フルショット時にも必要とされるが、アプローチショ 材として形成された請求項1記載のスリーピースソリッ 10 トなどのコントロールショットにおいて特に重要にな る。例えば、バンカー越えでグリーンエッジからカッ

【請求項3】 センターコアの硬度がJIS-C硬度4 5~80で、カバーの硬度がJIS-C硬度50~85 である請求項1又は2記載のスリーピースソリッドゴル フボール

【請求項4】 センターコアがポリブタジエンを主材と するゴム組成物からなる請求項1万至3のいずれか1項 記載のスリーピースソリッドゴルフボール。

【発明の詳細な説明】

[0001]

【産業上の利用分野】本発明は、センターコアと、中間 層と、カバーとからなるスリーピースソリッドゴルフボ ールに関し、更に詳述すると、打撃時のフィーリング、 コントロール性、及び耐久性に優れたスリーピースソリ ッドゴルフボールに関する。

[0002]

【従来の技術】従来、一般的に用いられているゴルフボールには、糸巻きゴルフボールとソリッドゴルフボールとがあり、近年ソリッドゴルフボールが主流となりつつあるが、その中でもコアとこれを被覆するカバーとから30なるツーピースソリッドゴルフボールが広く普及している

【0003】ツーピースソリッドゴルフボールは、飛距離及び耐久性に優れていることから多くのゴルファーに使用されているが、その反面糸巻きゴルフボールに比べて打撃時の打墜が硬く、球離れの速さからフィーリング、コントロール性に劣るという欠点がある。このため、フィーリング、コントロール性を重視するプロゴルファーや上級ゴルファーは糸巻きゴルフボール、特に軟らかいバラタカバーを用いた糸巻きゴルフボールを用いる場合が多い。しかし、糸巻きゴルフボールは飛距離及び耐久性の点でツーピースソリッドゴルフボールに劣るものである。

【0004】このように、ツーピースソリッドゴルフボールと糸巻ゴルフボールとは、互いに相反する性能を有しており、プレーヤーは自分の義俑や好みにより使用するゴルフボールを選択しているのが現状である。

【0005】現在、ソリッドゴルフボールにおいて、糸 に、上記中間層の比重をセンターコアの比重よりも小さ 巻ゴルフボールに近いフィーリングを実現するため、軟 く設定することにより、例えばセンターコアをJISー らかいタイプのツーピースソリッドゴルフボールが提案 50 C硬度45~80、カバーをJISーC硬度50~85

されている。このような軟らかいタイアのツービースソリッドゴルフボールを得るためには、軟らかいコアを用いることになるが、コアを軟らかくすると、反発性が低下して飛び性能が劣化すると共に、耐久性も著しく低下し、ツービースソリッドゴルフボールの特徴である優れた飛び性能及び耐久性が得られないばかりでなく、実際の使用に耐え難くなってしまう場合もある。

【0006】また、コントロール性はドライバーなどのフルショット時にも必要とされるが、アプローチショットなどのコントロールショットにおいて特に重要になる。例えば、バンカー越えでグリーンエッジからカップまでの距離が短い場合などは、プロ、アマチュアをとわず、ランの少ないボールを打ちたいと思うのは当然のことであり、このようなゴルフボールのコントロール性は、スピン特性に大きく依存すると考えられる。

【0007】この場合、比較的ロフト角の大きいクラブでフルショットした場合は、ボールそのものよりもクラブロフトの効果が大きく、おおよそほとんどのボールにスピンが利き、転がり過ぎることはほとんどない。しかし、30ヤード、50ヤードといった短い距離のアプローチショットを行う場合にはボールによって転がり、即ちコントロール性に大きな差が生じる。この差を生じる大きな要因は、基本的な構造によるところは少なく、カバー素材によるところが大きいと考えられる。しかしながら、ツーピースソリッドゴルフボールにおいて、このようなコントロール性を向上させるため、カバーを軟らかい案材で構成すると、飛距離が低下してしまう。

【0008】本発明は、上記事情に鑑みなされたもので、ソリッドゴルフボールの特徴である良好な飛び性能及び耐久性を劣化させることなく、フィーリング及びコントロール性を向上させ、トータルバランスに優れたソリッドゴルフボールを提供することを目的とする。

【0010】即ち、直径29mm以上、比重1.4未満のセンターコアの外周に、厚さ1mm以上、比重1.2未満、JIS-C硬度85以上の中間層を形成し、この中間層の外周を厚さ1~3mmのカバーで被覆すると共に、上記中間層の比重をセンターコアの比重よりも小さく設定することにより、例えばセンターコアをJIS-C硬度45~80、カバーをJIS-C硬度50~85

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に軟らかく形成しても飛距離や耐久性を低下させること なく、フィーリング及びコントロール性を向上させるこ とができ、またこの場合上記中間層を高反発性のアイオ ノマー樹脂を主成分とする樹脂を用いて形成することに より、飛距離や耐久性の低下を生じることなくより確実 にフィーリング及びコントロール性を向上させ得ること を見出し、本発明を完成したものである。

【0011】従って、本発明は、センターコアと、中間 層と、カバーとからなるスリーピースソリッドゴルフボ 1. 4未満、中間層が厚さ1mm以上、比重1. 2未 満、JIS-C硬度85以上、カバーが厚さ1~3mm であり、かつ上記中間層の比重がセンターコアの比重よ りも小さいことを特徴とするスリーピースソリッドゴル フボールを提供する。また、好適な実施態様として中間 層が高反発性アイオノマー樹脂を主材として形成された 上記スリーピースソリッドゴルフボールを提供する。

【0012】以下、本発明につき更に詳しく説明する。 本発明のスリーピースソリッドゴルフボールは、図1に 示すように、ボールの中心となるセンターコア1とボー 20 ル最外層のカバー3との間に比較的硬い中間層2を設 け、これらセンターコア1、中間層2及びカバー3の厚 さ、比重を特定範囲に設定したものである。

【0013】上記センターコア1は、直径29mm以 上、好ましくは29~37mm、比重1、4未満、好ま しくは1.05~1.38に形成する。直径が29mm 未満であると、相対的に中間層が厚くなりすぎ、反揺性 及びフィーリングが低下し、また比重が1.4以上であ ると、ボール重量が大きくなり過ぎ、ゴルフボールとし ての重量規定に適合したボールを構成することが困難に 30 なる。

【0014】ここで、ドライバー打撃時のように変形量 の大きなインパクトにおいて、プレーヤが感じるフィー リングは、このセンターコア1の硬度に大きく依存し、 この場合フィーリングはプレーヤのクラブヘッドスピー ドによって変化するものである。従って、このセンター コア1の硬度は対象プレーヤのヘッドスピードに応じて 設定されるべきもので、特に制限されるものではない が、一般的にはJIS-C硬度で45~80(センター コア表面)、特に60~80の範囲とすることが好まし 40 W.

【0015】このセンターコア1は、基材ゴムに共架橋 剤、過酸化物を配合した公知のゴム組成物を加熱・加圧 ・成型して形成することができる。

【0016】この場合、基材ゴムとしては、従来からソ リッドゴルフボールに用いられているポリブタジエンゴ ム或いはポリプタジエンゴムとポリイソプレンゴムとの 混合物などを使用することができるが、本発明において は、高反発性を得るためにシス構造を90%以上有する 1.4ーポリプタジエンゴムを用いることが好ましい。

【0017】共架橋剤としては、従来ソリッドゴルフボ ールには、メタクリル酸、アクリル酸等の不飽和脂肪酸 の亜鉛塩、マグネシウム塩やトリメチルプロバントリメ タクリレート等のエステル化合物が使用されており、本 発明においてもこれらを使用することができるが、反発 性の高さからアクリル酸亜鉛が好適に使用し得る。これ ら共架橋剤の配合量は、上記基材ゴム100重量部に対 し15~30重量部とすることが好ましい。

【0018】過酸化物としては、種々選定し得るが、ジ ールにおいて、センターコアが直径29mm以上、比重 10 クミルバーオキサイド或いはジクミルバーオキサイイド と1.1-ビス(t-ブチルパーオキシ)3.3.5-トリメチルシクロヘキサンとの混合物が好適である。そ の配合量は、基材ゴム100重量部に対し0.5~1重 **量部とすることが好ましい。**

> 【0019】なお、上記ゴム組成物には、更に必要に応 じ、比重調整に酸化亜鉛や硫酸パリウムなどを配合し得 るほか、老化防止剤を配合することができる。

> 【0020】上記中間層2は、厚さ1mm以上、好まし くは1.5~3.5mm、比重1.2沬満、好ましくは 0.9~1で上記センターコアの比重より小さく、J1 S-C硬度85以上、好ましくは85~100に形成す る。厚さが1mm未満であると反発性が低下して飛距離 の低下を招くことになり、また比重が1、2以上である と、相対的にセンターコアの比重を小さくしなければな らず、この場合ゴルフボールの慣性モーメントが大きく なってスピン特性が低下し、コントロール性を劣化させ ることになり、また比重がセンターコアの比重よりも大 きい場合も同様である。更に、JIS-C硬度が85未 満であると飛び性能の低下を招く。なお、この中間層2 の直径は、特に制限されるものではないが、38~41 mmとすることが好ましい、また、この中間層2と上記 センターコア1との比重差は、特に制限されるものでは ないが、0、1以上、特に0、1~0、5とすることが 好ましい。

【0021】この中間層2は、軟らかく形成したセンタ ーコア1の反発性の低下を補うためのもので、比較的硬 く(JIS-C硬度85以上)かつ反発性に優れた材質 で形成され、具体的には、ハイミラン1706、同16 05(三井・デュポンポリケミカル社製)、サーリン (デュポン社製)等のアイオノマー樹脂などが挙げら れ、これらの中でも特にハイミラン1706とハイミラ ン1605との1:1ブレンド物が好ましく用いられ る. なお、この中間層 2には、上記アイオノマー樹脂に 加えて重量調節剤として酸化亜鉛、硫酸バリウム等の無 機充填剤や着色のために二酸化チタン等の添加剤を添加 することができる.

【0022】上記カバー3は、厚さ1~3mm、好まし くは1.5~2.5mmに形成される。この場合、カバ -3の厚さが3mmを超えると反発性が低下し、一方1 50 mm未満であると、耐カット性等の耐久性が低下する。

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また、このカバー3の硬度は、特に制限されるものでは ないが、JIS-C硬度で50~85、特に60~85 の比較的軟らかい範囲に設定することが好ましく、これ により反発性(飛び性能)、耐久性及びコントロール性 のすべてを効果的に向上させることができる。

【0023】このカバー3は、ソリッドゴルフボールの カバー材として通常使用されるものを使用することがで き、特に比較的軟らかく(JIS-C硬度50~85) かつ高反発性を有するものが好適に用いられる。具体的 には、ハイミラン1650(三井・デュポンポリケミカ 10 フィーリング ル社製)、サーリン8120 (デュボン社製)等のアイ オノマー樹脂、又はこれらの混合物、ハイトレル404 7 (東レ・デュボン社製) 等のポリエステル系熱可塑性 エラストマー、バラタ樹脂などが好適に使用される。な お、必要に応じて上記樹脂に着色等のため無機充填剤を 添加してカバー3を形成することができる。

[0024]

【実施例】以下、実施例、比較例を示して本発明を具体 的に説明するが、本発明は下記実施例に制限されるもの てはない。

[実施例,比較例]表1に示した組成でセンターコア、 中間層、及びカバーを形成し、表2に示した性状のスリ ーピースソリッドゴルフボール(実施例1~6、比較例 1~3)を製造した。

【0025】この場合、センターコアは各成分を混練口 ールを用いて混練し、155℃で15分間加圧成形する ことにより形成し、また中間層は射出成形により、セン ターコアの外周を被って形成した。そして、この中間層 の外周に射出成形によってカバーを形成し、スリービー スソリッドゴルフボールとした。

【0026】得られた各ゴルフボールにつき、下記方法

6 によりスピン特性、フィーリング、飛び性能、耐久性を 評価した。結果を表2に示す。

スピン特件

ツルーテンパー社製スイングロボットを用い、ドライバ ーでヘッドスピード45m/s (表ではW1、HS45 と略記)及びサンドウェッジでヘッドスピード17、6 m/s (表ではSW., HS17.6と略記)で打撃 し、サイエンスアイ(ブリヂストン社製)でスピンを観 選した。

プロゴルファーにより打撃時の感触を下記基準で評価し

良好: 〇 普通: △ **劣る: ×** 飛び性能

上記スピン特性及びフィーリングを評価する際、打撃し たボールの飛距離を測定し、下記基準に従って総合的に 評価した。

20 優る: 〇 普通: △ 劣る: × 耐久性

> フライホイール打撃M/Cを用い、ヘッドスピード38 m/sで繰返し打撃して、ボールが破壊するまでの打撃 回数の多少により評価した。

良好: 〇 普通: △ 劣る: × 30 [0027]

【表】】

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	9								10	
			実	8	E .	Ø		比	较	<i>6</i> 4
		1	2	3	4	5	6	1	2	3
セン	外 (mm)	31.52	35.28	35.28	35.28	35.29	36.40	27.68	35.24	31.62
9	硬度 (JIS - C)	66	66	66	79	66	66	68	73	88
コア	比 童	1.36	1.24	1.24	1.19	1.16	1.07	1.56	1.19	1.35
ф	厚 さ (mm)	3.4	1.7	2.2	2.2	1.7	2.0	5.7	1.8	1.6
H	硬 度 (JIS - C)	91 .	91	91	91	91	91	91	82	91
[ER]	比 篮	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.97	0.95
靥	外 後 (mm)	38.35	38.73	39.65	39.66	38.73	40.40	39.00	38.91	34.56
カ	厚 さ (mm)	2.2	2,0	1.5	1.5	2.0	1.8	1.8	1.9	4.0
バ	比 重	0.97	0.97	0.97	1.10	1.13	0.97	0.97	1.10	0.97
1	硬 (JIS - C)	82	82	82	61	78	82	82	61	82
製	外 径 (mm)	42.68	42.67	42.67	42.70	42.70	44.00	42.65	42.63	42.65
픎	重量	45.50	45.45	45.50	45.55	45.53	45.60	45.50	45.55	45,50
性能	W1. スピン HS45 特 性	3300	3020	3030	3920	3600	3030	3500	3600	3250
	(rpm) SW. HS17.6	3900	4000	4300	6390	5800	4100	4100	4050	3500
	フィーリング	Δ	0	0	Δ	0	0	×	0	0
	飛び性能	0	0	0	0	Δ	Ō	× .	×	×
	耐久性	0	0	0	0	0	0	0	0	0

【0029】表2の結果から明らかなように、本発明の スリーピースソリッドゴルフボールは、良好なフィーリ ング及びコントロール性 (スピン特性) が得られるよう にセンターコア及びカバーを軟らかく形成しても、飛び 40 【図面の簡単な説明】 例能や耐久性を劣化させることなく、バランスの優れた ゴルフボールを得ることができることが確認された。 [0030]

O

【発明の効果】以上説明したように、本発明のスリービ ースソリッドゴルフボールによれば、フィーリング及び コントロール性を向上させるためにセンターコア及びカ* *バーを比較的軟らかく形成しても、飛び性能及び耐久性 を劣化させることがなく、トータルバランスに優れたゴ ルフボールを構成することができる。

【図1】本発明スリーピースソリッドゴルフボールの一 例を示す概略断面である、

【符号の説明】

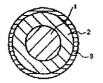
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JAMES S. FALCONE, JR. SCOTT D. BOYCE The PQ Corporation

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The term silicone denotes a synthetic polymer $(R_n SiO_{(4-nu2})_m)$, where n=1-3 and $m\geq 2$. A silicone contains a repeating silicon—oxygen backbone and has organic groups R attached to a significant proportion of the silicon atoms by silicon—carbon bonds. The term silicone has no place in scientific nomenclature, although it was originally introduced under the supposition that compounds of the empirical formula RR'SiO were analogous to ketones (1); later it was used to describe related polymers (2). In commercial silicones most R groups are methyl; longer alkyl, fluoroalkyl, phenyl, vinyl, and a few other groups are substituted for specific purposes. Some of the R groups can also be hydrogen, chlorine, alkoxy, acyloxy, or alkylamino, etc. These polymers can be combined with fillers, additives, and solvents to result in products loosely classed as silicones.

Silicones have an unusual array of properties. Chief among these are thermal and oxidative stability and physical properties little affected by temperature. Other important characteristics include a high degree of chemical inertness, resistance to weathering, good dielectric strength, and low surface tension. As the general formula implies, the molecular structure can vary considerably to include linear, branched, and cross-linked structures. These structural forms and the R groups provide many combinations of useful properties that lead to a wide range of commercially important applications. Silicones include fluids, resins, and elastomers. Many derived products, eg, emulsions, greases, adhesives, sealants, coatings, and chemical specialties, have been developed for a large variety of uses (3).

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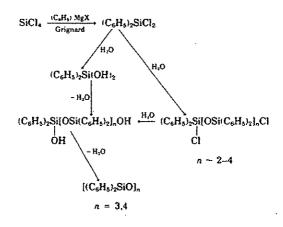
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Silicones are unique among the important commercial polymers in both basic chemistry and variety of industrial applications. Scientific interest in silicones can be traced to the previous century, but industrial development did not begin until the early 1930s (4.5). The methylsilicones, which are of greatest economic and technical importance, were initially chosen for investigation and development because of their stability and inertness. Interest grew as the full spectrum of properties afforded by this unique class of synthetic materials was recognized.

Silicones were the first useful polymers based on organometallic chemistry. Scientific development began with the isolation of silicon metal and preparation of silicon tetrachloride (1828), ethyl silicate (1845), and trichlorosilane (1857) and the first syntheses of R—Si—X compounds, such as tetraethylsilane from silicon tetrachloride and diethylzinc (1863); silane, SiH₄, was first prepared in 1912.

In 1904 Kipping began his classical studies in organosilicon chemistry with the synthesis of several R—Si—X compounds by Grignard procedures. During the next three decades he elucidated much of the basic chemistry of organosilicon intermediates, substituted silanes, and low polymeric siloxanes. Most of his work was done on aryl-substituted chlorosilanes. Hydrolysis frequently led to isolable and identifiable intermediates whose properties could be studied. For example, aryl-substituted hydroxy-functional silicon compounds were found to be orders of magnitude more reactive than the analogous carbinols, and they frequently condensed spontaneously to form —Si—O—Si—ring or chain compounds.

Isolation of a monomer containing a silicon-oxygen double bond such as $(C_6H_5)_2Si=O$ could not be predicted. By analogy with ketones, such hypothetical monomers were called silicones by Kipping. However, his silicanediols, eg, $(C_6H_5)_2Si(OH)_2$, could not be dehydrated as initially expected, but always condensed to higher molecular weight Si-O-Si compounds. These structures were called silicones. Although this term is still used today, its meaning has changed. It is now used to designate complex polymeric siloxane products, often undefinable in exact scientific terms, frequently mixtures of many components, and in many cases useful in practical ways. The principal thrust of Kipping's research is shown below; the direction of future development of the field can be inferred.



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Several U.S. industrial laboratories became interested in the field, including the Corning Glass Works, the Mellon Institute, and the General Electric Co. At the same time, work was initiated in the USSR. All these laboratories investigated the preparation of high molecular weight organo-substituted silicon polymers with unusual properties.

In the United States, Corning Glass Works pioneered commercial work on organosilicon polymers with the objective of developing resins as varnishes and partners for glass fiber in high temperature electrical insulation. General Electric had similar interests, but first chose to work with silicate esters. Somewhat later, Union Carbide Corp. began a program of organometallic research that included organosilicon chemistry. Expansion to pilot plant production by Corning Glass and General Electric was followed by the formation of the Dow Corning Corp. in 1943, a joint effort by Corning Glass and Dow Chemical Co.

Military uses dominated early product development in the United States. Silicone fluids were used for damping aircraft instruments, antifoams in petroleum oils, and greases used as ignition sealing compounds. Silicone resins were employed as components of insulation for motors, and silicone rubber for searchlights and turbosupercharger gaskets. After World War II, civilian uses followed these patterns, but expanded gradually to include release agents for molding rubber; water repellents for textile, paper, and masonry; ingredients for paints, lubricants, and automobile and furniture polishes; and others. Pharmaceutical applications for organosilicon materials began in the early 1950s (6). In the 1960s novel silicone elastomers, ie, room-temperature-vulcanizing (RTV) rubbers, which are sold as pastelike liquids that cure in situ without heat, were introduced. These RTV products quickly became a significant part of the total silicone product mix. Today they are extensively used in diversified applications as adhesives, sealants (qv), gaskets, coatings (qv), encapsulants, potting compounds, and molding materials (7) (see also ADHESIVE COMPOSITIONS; EMBEDDING; ELECTRONICS APPLICATIONS).

Work in the USSR first led to the development of silicone resins that were produced industrially by the end of the 1930s.

Nomenclature

Polymer nomenclature is inherently complex and difficult to use; that of silicones is simplified by the use of the letters M, D, T, and Q to represent monofunctional, difunctional, trifunctional, and quadrifunctional monomer units, respectively (8). Primes, eg, D', are used to indicate substituents other than methyl; symbols are shown in Table 1. The meaning of the primes must be specifically indicated in the text. The MDTQ nomenclature can be used to identify silicones (polysiloxanes) with as little ambiguity as the more conventional systems. Proper nomenclature follows IUPAC rules, but in the written or spoken language of the industry, it is much more common, for example, to see D_4 , methyltetramer, or simply tetramer than the proper octamethylcyclotetrasiloxane (9,10). In another example, $(CH_3)_3SiOSi(CH_3)_2OSi(C_6H_5)[OSi(CH_3)_3]_2$ is designated MDT'M₂, where T' is $C_6H_5SiO_{1.5}$. Table 2 shows the various ways of identifying siloxanes.

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Table 1. Formulas and Symbols for Silicones*

Formula	Functionality	Symbol
·CH ₃ 1 ₃ SiO _{6.5}	mono	М
(CH _c),SiO	di	D
CH ₁ SiO _{1.5}	tri	T
CH3"C6H5ISiO	đì	D.
(C ₄ H _{5/2} SiO	di	D.
(CH,)(H)SiO	di	D.
SiO ₂	quadri	Q
° Ref. 8.		

Table 2. Identification of Siloxanes*

Ch. t.l		MDT	_
Chemical name	Structural formula	formula	Common name
hexamethyldisiloxane	(CH ₃) ₃ SiOSi(CH ₃) ₃	MM	mono
octamethyltrisiloxane	(CH ₂) ₃ SiOSi(CH ₂) ₂ OSi(CH ₃) ₃	MDM	linear trimer
decamethyltetrasiloxane	(CH ₃) ₃ SiO(Si(CH ₃) ₂ O) ₂ Si(CH ₃) ₃	MD_2M	linear tetramer
octamethylcyclotetra- siloxane	(CH ₃) ₂ Si—O—Si(CH ₃) ₂ O O	D ₄	cyclic tetramer
	(CH ₃) ₂ Si OSi(CH ₃) ₂		
octaphenylcyclotetra- siloxane	$(C_aH_s)_2Si - O - Sit(C_eH_s)_2$ O O	D;	cyclic phenyl- tetramer
	$(C_6H_5)_2Si-O-Si(C_6H_5)_2$		
2,4,6,8-tetramethyl- 2,4,6,8-tetraphenyl- cyclotetrasiloxane	(CH ₃)(C ₆ H ₅)Si—O—Si(CH ₃)(C ₆ H ₅)	D;	cyclic methyl- phenyl- tetramer
	$(CH_3)(C_6H_5)Si - O - Si(CH_3)(C_6H_5)$		
methyltris/trimethyl- siloxy/silane	[(CH ₃) ₃ SiO] ₃ SiCH ₃	M_5T	
1.1,1,3.5,5,5-heptamethyl- trisiloxane	(CH ₃) ₃ SiOSi(H)(CH ₃)OSi(CH ₃) ₃	MD'M	
1,1,3,5,5-pentamethyl-	$(CH_3)_2(C_6H_5)SiOSi(CH_3)(C_6H_5)$	M'D'M'	
1,3,5-triphenyltri- siloxane	OSi(C ₆ H ₅ HCH ₃) ₂		

^o Refs. 9, 10 and 20.

Structure and Properties

Silicone properties can be interpreted in terms of structural bond concepts (11-13). The silicon-oxygen chain that constitutes the backbone of these polymers is predominantly responsible for their uniqueness. A segment of methyl-siloxane chain is shown below (13):

Commonly accepted bond angles are $C-Si-C=-112^\circ$, $Si-O-Si=143^\circ$, and $O-Si-O=110^\circ$; bond lengths are Si-C=0.188 nm and Si-O=0.163 nm (5,14,15). The siloxane chain flexes, and rotation is fairly free about the Si-O axis. especially with small substituents, eg. methyl, on the silicon atoms (16). Rotation is also free about the Si-C axis in methylsilicon compounds. As a result of the freedom of motion, the intermolecular distances between methylsiloxane chains are greater than between hydrocarbons, and intermolecular forces are smaller (17). The small rotational barriers contribute to properties such as low modulus, low glass-transition temperature, and high permeability. The relationships between ring and chain forms in siloxane systems can be explained by the high flexibility of the chains.

Further structural considerations explain the weak temperature dependence of many physical properties. The preferred conformation for methylsiloxane chains is the trans form, but the large difference between successive bond angles in the chain causes this conformation to be of low spatial extension. Greater extension requires an increase in the number of higher energy (gauche) states, resulting in a greater distance between the ends of methylsiloxane chains at higher temperatures. Thus an increasing molecular entanglement compensates for the normal increase in molecular mobility with increasing temperatures. The viscosity of a simple methylsilicone fluid, for example, changes little with temperature, in contrast to hydrocarbon polymers, which have a stiffer structure (5,12,18).

Silicone behavior of this kind used to be explained on the basis of a regularly coiled, flexible helical structure that tended to relax with increasing temperatures. This view is now out of date, having been superseded by what has been discussed above (5,13,14).

Differences between silicon and carbon chemistry can be explained by electronegativity and orbital bonding effects. Silicon is more electropositive than carbon. Bonds between silicon and Cl, N, O, and S are more ionic and have higher energies than those to carbon. Analogously, bonds between silicon and C and H have lower energies than those to carbon.

Unlike carbon, silicon has available d orbitals. Electrons in these d orbitals can participate in bonding with π electrons from other atoms. The resulting $d\pi$ - $p\pi$ involvement is often consistent with partial double-bond character (19-22).

The influence of the orbital effect is usually stronger than that of the electronegativity. Accordingly, the oxygen atom in ethers is more basic than the oxygen in siloxanes. Similarly, the rate of electrophilic, eg, dichlorocarbene, addition to $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2$ is about twice that for $(\text{CH}_3)_3\text{SiCH}=\text{CH}_2$. In the absence of orbital effects, electronegativity effects explain behavior, eg, the greater basic character of nitrogen in $(\text{CH}_3)_3\text{SiCH}_2\text{NH}_2$ over nitrogen in $(\text{CH}_3)_2\text{NH}_2$.

The characteristic bonds of silicones are those to oxygen and to carbon. The nature of the Si—O bond is influenced by the electropositive character of silicon, which has a value of 1.7 in Pauling's scale of electronegativities (23), and by the availability of the vacant d orbitals in silicon for dative bonding. The Si—O bond is ca 50% ionic, with silicon being the positive member. It has a high heat of formation of 452 kJ/mol (108 kcal/mol) and is resistant to homolytic cleavage. However, it is susceptible to heterolytic cleavage, ie, to attack by acids and bases. In this respect the —Si—O—Si—O— backbone of silicones is very different from the —C—C—C—C—backbone of hydrocarbon polymers (24).

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The Si—C bond is slightly ionic, ie. 12% on the basis of Pauling's electronegativity, again with silicon being positive. The heat of formation is ca 318-356 kJ mol (76-85 kcal mol), which is almost as high as for the C—C bond. It may or may not be susceptible to heterolytic cleavage, depending on the substituents on the carbon. Chloromethyl, cyanomethyl, or even phenyl groups are more easily cleaved from silicon by water, acids, or bases than are methyl groups.

The Si—Cl bond is also important in silicone chemistry. Silicones are usually made from organochlorosilanes. The first step is a hydrolysis reaction. Such reactions occur very fast compared with hydrolyses of corresponding alkyl halides:

$${}^{1}CH_{3}{}^{1}{}_{3}SiCl + H_{2}O \xrightarrow{\text{very fast}} (CH_{3}{}^{1}{}_{3}SiOH - HCl$$

$$(CH_{3}{}^{1}{}_{3}CCl + H_{2}O \xrightarrow{\text{slow}} (CH_{3}{}^{1}{}_{3}COH + HCl$$

Here the hydrogen in SiOH is more acidic than in COH. A hydroxyl group attached to silicon is generally referred to as a silanol. Most silanols are unstable and readily condense (with the elimination of water) to form siloxane linkages, ie, Si—O—Si.

The Si—H bond is much more reactive and susceptible to heterolytic cleavage than its C—H counterpart. Silane, an extreme example, is spontaneously flammable in air and readily hydrolyzed by water, whereas methane is comparatively inert. Under certain conditions the Si—H bond adds across a carboncarbon multiple bond. This has become an important synthetic pathway in organosilicon chemistry (19,20).

Until recently, it was supposed that silicon does not form double bonds per se. However, recent work has now confirmed the synthesis of structures with a silicon double bond (25–27).

Process

Silica, a material of mineral origin, is the natural source of silicon. It is usually reduced in an electric furnace process to silicon metal.

Silicon is treated with an organic halide to form organohalosilanes. The first industrial method used a Grignard reagent:

$$Si + 2 Cl_2 \xrightarrow{\Delta} SiCl_4$$

$$SiCl_4 + 2 RMgX \longrightarrow R_2SiCl_2 + 2 MgClX$$

This method was operationally difficult and costly. A direct process (28,30-32) provided the impetus for the commercial manufacture and marketing of silicones.

where RCl is usually methyl chloride.

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Hydrolysis of organochlorosilanes gives siloxane structures, which are the basis of silicone products:

$$2 R_2 SiCl_2 = 4 H_2O \longrightarrow 2 |R_2 SiOH)_2| = 4 HCl$$
unstable
$$2 H_2O = \begin{pmatrix} R & R \\ \vdots & \vdots \\ -Si-O-Si-O \\ \vdots & R \end{pmatrix}$$

Many silicone producers make most of the methyl chloride they need from methyl alcohol and HCl obtained from the hydrolysis of organochlorosilanes.

Silicas, particularly fumed silicas, are the principal fillers used to reinforce siloxane polymer systems in silicone elastomer formulations. Fumed silica is made by carefully controlled combustion of selected chlorosilanes.

The flow sheet of a generalized silicone process is shown in Figure 1. Silicon ore is a purchased raw material. Purchases of methyl chloride can be offset by recycling HCl. Not all producers run all the processes indicated. Some are selective and even purchase key intermediate siloxanes.

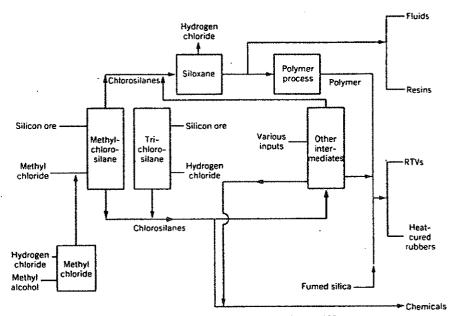


Fig. 1. Flow sheet of a silicone manufacturing facility. RTVs are room temperature vulcanizates.

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The main by-product of silicone manufacture is HCl. Silicone and HCl are made in almost equal amounts. Even allowing for HCl recycle through the methyl chloride process, large amounts often remain as waste to be treated and disposed of in an environmentally responsible manner.

Silanes

Organohalosilanes give siloxanes upon hydrolysis. Organic radicals, attached to silicon by hydrolytically stable linkages, survive these hydrolyses and thereby become a part of the siloxane product. The widespread commercial usefulness of silicone products is due to the economic manufacture of organosilanes (28).

Grignard synthesis was the traditional method. It is no longer commercially employed for methylchlorosilanes, but remains of wide preparative value for specialty intermediates and laboratory work. Silicon tetrachloride gives a mixture of alkyl- or arylchlorosilanes,

where R is an alkyl or aryl group. Mono-, di-, and trichlorosilanes can serve as starting materials for the preparation of mixed alkyl- or arylchlorosilanes.

$$RSiCl_3 + R'MgX \longrightarrow MgXCl + RSiR'Cl_2 + RSiR'_3Cl + RSiR'_3$$

Ethers such as ethyl ether, dibutyl ether, or tetrahydrofuran are the best solvents for Grignard synthesis of chlorosilanes; ethylene glycol ethers and diethylene glycol ethers are sometimes effective solvents.

Alkali metal and alkylmetal syntheses and metal exchange methods are used for the small-scale preparation of special intermediates.

SiCl₄ + RX + 2 Na (or Li)
$$\longrightarrow$$
 RSiCl₃ + NaCl + NaX
SiCl₄ + RNa (or Li) \longrightarrow RSiCl₃ + NaCl
RSiCl₃ + LiR' \longrightarrow RR'SiCl₂ + LiCl
RSiCl₃ + 2 Na \longrightarrow RSiCl₂Na + NaCl
RR'SiCl₂ + NaCl

Organolithium compounds are more reactive than Grignard reagents; organosodium and organopotassium compounds are still more reactive. Organozinc, organoaluminum, organomercury, and organocadmium compounds are used only in special cases (19). The reaction of silicon tetrafluoride with alkyl or aryl aluminum halides is widely applicable to the preparation of organosilicon halides (29).

The direct process, described previously, is the basis of commercial production (30-32). It avoids the use of highly reactive Grignard and alkylmetal re-

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agents, often difficult to prepare and hazardous to store, and of large amounts of volatile and flammable solvents. It is readily adaptable to large-scale and continuous or semicontinuous operations. First methylchlorosilanes and then phenylchlorosilanes were prepared by this route; some ethylchlorosilanes have been made in Europe.

Methylchlorosilanes

Methylchlorosilanes are the starting materials for methylsilicones. They are made industrially by the copper-catalyzed exothermic reaction of methyl chloride with silicon at ca 300°C (9,30,33-37).

$$\pi(CH_3Cl + Si) \xrightarrow[-300^{\circ}]{CH_3} (CH_3)_2SiCl_2, \ CH_3SiCl_3, \ (CH_3)_3SiCl_3$$

To minimize high temperature side reactions the heat generated is removed with the help of stirred or fluidized beds (38–40). The reaction produces chlorosilanes, chlorodisilanes, hydrocarbons, and complex silicon compounds (Table 3). Under proper control the principal product is dimethyldichlorosilane; yields of 85–90% have been reported in laboratory operations. The crude product stream is separated, and the principal components are purified by fractional distillation in a system of continuous columns supplemented by batch columns for minor products.

Table 3. Properties of Methylchlorosilanes*

Compound	Boiling point, 'C	Density d ²⁶ , g cm ³	Refractive index. กรื ⁶	Assay, %
(CH ₃)SiCl ₃	66.4	1.273	1.4088	95-98
(CH ₃) ₂ SiCl ₂	70.0	1.067	1.4023	99-99.4
CH ₂) ₃ SiCl	57.9	0.854	1.3893	90-98
(CH ₂)SiH(Cl) ₂	41.0	1.110	1.3982	95-97
(CH ₃) ₂ SiH(Cl)	35.0	0.854	1.3829	

e Refs. 19, 20, and 35.

The first plant for commercial production of organochlorosilanes was built by Dow Corning Corp. in 1943. Silicon tetrachloride was converted to methylchlorosilanes by a Grignard reaction. The manufacture of methylchlorosilanes by the direct process was introduced by General Electric in 1947 and has become the standard of the industry (30–32). This reaction was originally carried out in batch or semicontinuous reactors. Ground silicon metal and copper catalyst were being charged continuously or intermittently with methyl chloride near 300°C and slightly above atmospheric pressure. After most of the silicon was consumed, the reaction rate decreased, and the spent solids were discharged and replaced with fresh silicon. The emerging chlorosilane vapors were condensed and separated from unreacted methyl chloride, which could be recycled. After filtration to remove entrained solids, the chlorosilanes were fractionated to provide individual methylchlorosilanes for hydrolysis to siloxanes.

Today, the process is operated in a fluid-bed system on a continuous basis (39) (Fig. 2). Silicon metal is crushed and ground to a fluidizable particle size

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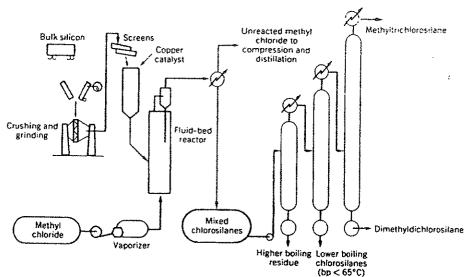


Fig. 2. A typical flow diagram for methylchlorosilane production (41).

range and mixed with finely divided copper catalyst and sometimes small amounts of certain additives. Catalyst and additives can also be fed separately. Liquid methyl chloride, under pressure, is vaporized and passed through a bottom diffuser plate and up through the bed at velocities sufficient to maintain the bed in a fluidized condition. Although residence times are short, eg. a minute or less, conversions of 25–90% (based on methyl chloride) are common. The temperature is controlled with a heat-transfer medium circulating through the reactor jacket or internal cooling coils to remove the heat of reaction. Entrained solids are removed with cyclone separators, filters, scrubbers, or settling chambers, and the crude chlorosilanes are condensed and stored. The composition of the crude mixture varies, depending on conditions, but generally falls within the ranges given below:

dimethyldichlorosilane >50%
methyltrichlorosilane 10-30%
methyldichlorosilane <5%
trimethylchlorosilane other monosilanes
higher boiling residue vp to 15%

The mixture is separated by fractional distillation.

The highest demand is for dimethyldichlorosilane, which is a raw material for silicone fluids, elastomers, and resins; operating conditions are chosen to optimize its formation. Of these conditions the catalyst is most important, followed by particle size distribution, the condition of the particles in the bed, and methyl chloride quality.

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The most widely employed catalyst is copper powder, usually in the amount of 10% of the weight of the silicon metal. Other metals, particularly silver, are also useful; copper-silver alloys were studied. Some investigators prefer cuprous chloride over metallic copper; partial oxidation of the copper is also effective (35).

Highly purified silicon metal (semiconductor grade) reacts very sluggishly with alkyl chlorides. Commercial-grade silicon (ca 98%) is much more reactive. To be fully effective, it must be intimately mixed with powdered copper. Small amounts of certain other metals, such as aluminum and zinc, increase catalyst activity; lead, however can act as a poison (12,35,42,43).

After an induction period the reaction progresses, and copper, carbonaceous degradation products, and other nonvolatile components accumulate in the bed. Fresh silicon and copper can be added during the course of a run. Reaction occurs at the surface of the bed particles where the copper, present as an alloy with silicon, acts as catalyst. As silicon is consumed from the surface, it is replenished by diffusion. Changes in composition and carbonaceous buildup eventually deactivate the catalyst. Silicon conversions up to 90% can be attained (35).

The selectivity of the reaction for dimethyldichlorosilane is usually determined by the ratio (T:D) of methyltrichlorosilane to dimethyldichlorosilane produced; ratios of 0.1–0.2 are preferred. During the induction period the reaction rate is low and the T:D is high (eg, 0.6) (Fig. 3). As the silicon conversion increases, the reaction rate advances through a maximum; the T:D should then reach preferred values, but increases as the bed ages. It is desirable to have a short induction period, low overall T:D values, and acceptable rates through a run (44).

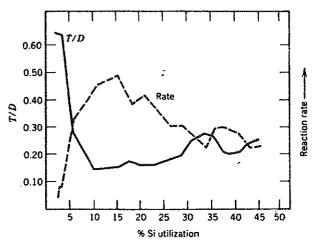


Fig. 3. T:D and rate behavior during a direct process batch reaction. Adapted from Ref. 44.

The mechanism of the direct process was studied in detail (eg, 45,46); freeradical processes were initially assumed to play important roles. Temperatures above 250°C, which usually prevail in direct process reactors, are adequate to nt re us

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res to generate free radicals. The formation of most products can be explained by freeradical dissociations, disproportionations, and recombinations. Copper is catalytically effective because of its ability to facilitate radical transport.

$$CH_{3}CI - Cu \longrightarrow CH_{3} - CuCI$$

$$CH_{3} + Cu \longrightarrow CH_{3}Cu$$

$$Si + CH_{3}Cu \longrightarrow -SiCH_{3} + Cu$$

$$Si + CuCI \longrightarrow -SiCI + Cu$$

$$-SiCH_{3} + CuCI \longrightarrow CISiCH_{3} + Cu, etc$$

Although the complexity of the direct process, particularly the many byproducts formed, suggested important roles of free radicals to earlier investigators, this view is not held today. A pure free-radical mechanism is at odds with later experiments, which gave negative results for radicals.

More recently, different explanations are based on chemisorption phenomena rather than radical transfer. Phase relations studied in copper—silicon alloys have focused on reactive phases, particularly the so-called η phase, of composition Cu₃Si. Charge separation within such phases provides active surface areas where polar (and easily polarizable) molecules such as methyl chloride are strongly adsorbed (47). The initial steps in this mechanism involve neutralization of partial ionic charges through chemisorption.

The transition state is highly oversimplified, but indicates the dissociative adsorption of methyl chloride. This is a key step in the overall process for transferring CH₃ and Cl groups to silicon. It takes place at active surface centers and involves a chemisorbed layer (12,48,49).

The catalytic effectiveness of copper in the direct process with methyl chloride is related to the ability of methyl chloride to oxidize copper and the ability of silicon to reduce copper salts. Furthermore, silicon bonds may be weakened by alloying with copper. The induction period can be considered a time for the removal of interfering coatings and chlorination; CuCl is the important species for copper deposition at the silicon surface, but CuCH₃ may also play a role. Chlorosilane formation is optimal when catalyst and other beneficial elements are appropriately alloyed with silicon, particularly at active sites. As silicon is consumed, proper compositional relationships at the surface are maintained by diffusion (12,49–51).

The beneficial effects of various metals present along with copper may provide some explanation. Reactive electropositive metals forming stable chlorides,

eg. Al, Ca. and Mg, reduce the induction period. Additive metals. like Zn and Cd, may improve process performance by forming fluxes to remove and minimize harmful surface contaminants, lower surface tension, and aid fusion and diffusion. The reported effects of promoter metals like Sb. Bi. and As are less clearly understood, but may depend on affecting redox behavior.

Process performance can be excellent when small amounts of metals from the classes mentioned above are present. Desirable percentages based on silicon are reported to be Cu = 5-10, electropositive metal = 0.1-1, flux metal = 0.1-1, and promoter metal = 0.001-0.005. A process evaluation using Cu, Al, Zn, and Sb found inferior performance when any one metal was missing (12,52).

Recent industrial patents have disclosed highly selective and reactive direct process contact mass configurations; critical ratios of catalyst, additive, and promoter metals are given. Most of this work focuses on the incorporation of tin (53-59).

Small amounts of other metals (or salts) in Cu—Si alloys or contact masses may alter lattice parameters sufficiently to increase or reduce chemisorption and polarization. By-products, eg, hydrocarbons, hydrogen, and carbonaceous deposits, may be due to the decomposition of methyl chloride. Aluminum chloride is an example of a catalytic species for such side reactions (12).

The production of the individual compounds in this complex reaction mixture cannot be balanced with demand. Several interconversion processes can be used to achieve a balance.

Redistribution

$$(CH_3)SiCl_3 + (CH_3)_3SiCl \xrightarrow{\text{catalyst}} 2 (CH_3)_2SiCl_2$$

Cleavage

Aluminum chloride catalyzes the redistribution reaction, and Si—H compounds promote catalysis (60,61). At equilibrium the mixture contains ca 70 wt % $(CH_3)_2SiCl_2$. Amines catalyze the cleavage of disilanes by HCl. This type of cleavage reaction can be important because the high boiling residue from the direct process is usually on the order of 4% of the $(CH_3)_2SiCl_2$ formed and consists of ca 90% disilanes. Other reactions (62) of possible utility include disproportionation to methylchlorosilanes and polysilanes; hydrogenolysis, a route giving good yields of $(H)(CH_3)_2SiCl_3$; and cleavage in the presence of an organic halide to obtain organochlorosilanes with substituents other than methyl groups (63). Highboiling disilane fractions can be cracked, using aryl halides or halogens and a catalyst, to yield monosilanes suitable for direct hydrolysis or for conversion to other intermediates (64,65).

The processing equipment is constructed from steel. Chlorosilanes react with zinc, tin, magnesium, and aluminum at elevated temperatures; alloys of these metals must be avoided. Corrosion is a serious problem. Chlorosilanes escaping from the system are hydrolyzed by the moisture in the atmosphere with the liberation of corrosive hydrogen chloride and the formation of a polymer get

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Systems must be designed to minimize internal release of water from condenser tubes, steam bundles, jackets, and tracers because of the danger of massive exothermal reactions. Because of the hazards associated with handling chlorosilanes, careful design and maintenance are essential to all facilities used in their manufacture (66).

Other Chlorosilanes and Derivatives

Ethyl- and phenylchlorosilanes are made by the same kind of direct reaction as the methylchlorosilanes from an organic chloride and silicon. Treatment of silicon with chlorobenzene at ca 550°C over a copper or silver catalyst gives phenyltrichlorosilane and diphenyldichlorosilane with trace amounts of other chlorosilanes. With a copper catalyst, feeding hydrogen chloride promotes the reaction. In addition to the difficulties of operating at high temperatures, the process is complicated by the thermal degradation of the chlorobenzene. The reaction product is fractionated to recover first unreacted chlorobenzene for recycle and then the volatile by-products; the phenylchlorosilanes are purified by vacuum fractionation (35,67).

Except for the methyl, ethyl, and phenyl systems, the direct reaction is inefficient for making organochlorosilanes because of extensive degradations.

Phenylchlorosilanes can also be prepared by a Grignard process, related organometallic processes, and condensation of Si—H compounds with benzene.

$$CH_3SiCl_3 + C_6H_5MgBr \longrightarrow (CH_3)(C_6H_5)SiCl_2 + MgBrCl$$

$$CH_3(H)SiCl_2 + C_6H_6 \xrightarrow{BCl_1} (CH_3)(C_6H_5)SiCl_2 + H_2$$

The phenyl groups in phenylchlorosilanes can be chlorinated (20).

Trichlorosilane is made by the reaction of elemental silicon with anhydrous hydrogen chloride at elevated temperature:

Condensation reactions give phenylchlorosilanes (68,69).

$$HSiCl_3 + C_6H_6 \xrightarrow{BCl_3} C_6H_5SiCl_3 + H_2$$

Vinylchlorosilanes are made similarly from vinyl chloride in a hot tube without a catalyst (70),

$$(CH_3)_2(H)SiCl + CH_2 = CHCl \xrightarrow{500^{\circ}C} HCl + (CH_3)_2(CH_2 = CH)SiCl$$

or by the addition of Si-H compounds to acetylene,

$$(CH_3)(H)SiCl_2 + C_2H_2 \xrightarrow{Pt} (CH_3)(CH_2=CH)SiCl_2$$

This type of addition reaction to carbon-carbon multiple bonds is termed hydrosilation (71).

Hydrosilation reactions are widely used for the preparation of silanes, in-

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cluding many important organofunctional species. The reaction can be initiated by heat, light, and radiation, or it can be catalyzed by peroxides, bases, and noble metals. Catalysis by platinum (homogeneous and heterogeneous forms) is usually preferred; chloroplatinic acid is frequently employed (72). Catalysis by platinum is not always effective.

$$(CH_3)SiH_1CI_{12} - CH_2 = CHCF_3 \xrightarrow{P_1} (CH_3)(CF_3CH_2CH_2)SiCI_2$$

 $(CH_3)SiH_1CI_{12} + CH_2 = CHCN \xrightarrow{base} (CH_3)(CNCH_2CH_2)SiCI_2$

The vinyl compounds are vehicles for incorporating organofunctionality into siloxane compositions. Competitive reactions reduce hydrosilation yields. The platinum-catalyzed addition of silicon hydrides to 3-chloropropene, for example, gives both 3-chloropropyl and propyl derivatives (19,20,67).

Silicon hydrides are thus important intermediates. Organosilicon hydrides are obtained as by-products of the direct process or by the reduction of organohalogenosilanes. The silicon-hydrogen bond is stable in these compounds as pure liquids, in aprotic solvents, and even in protic solvents in the absence of acidic or basic catalysts. With protic solvents, in the presence of Lewis acids or strong nucleophiles, hydrogen is evolved.

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However, methylhydrogenchlorosilanes, eg, (CH₃)SiH(Cl)₂ and (CH₃)₂SiH(Cl), can be hydrolyzed to give silicone fluids without the loss of (reactive) hydrogen. Most organosilicon hydrides are easily halogenated, in some cases with explosive violence. Halogenation is therefore carried out in nonpolar or nonreactive polar solvents at low temperatures. The reactivity decreases from Cl2 to Br2 to I2 and with substitution on silicon (19,35,67).

The hydrolyzable chlorine groups in chlorosilanes can be substituted to give derivatives that are similarly hydrolyzable, but do not yield HCl as a by-product. This reduces corrosion and aids the preparation of reactive silicone compositions and of siloxanes that are unstable in the presence of strong acids. Alkoxylation, acyloxylation, and amination are employed for commercial products.

Alkoxylation

$$(CH_3)_2SiCl_2 + 2 CH_3OH \longrightarrow (CH_3)_2Si(OCH_3)_2 + 2 HC1$$

Acyloxylation

$$CH_3SiCl_3 + 3 (CH_3CO)_2O \longrightarrow CH_3Si(OCCH_3)_3 + 3 CH_3CCI$$

Amination

$$2 (CH_3)_3SiCl + 3 NH_3 \longrightarrow [(CH_3)_3Si]_2NH + 2 NH_4Cl$$

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Similar reactions lead to substitution by amides, ketoximes, and other active hydrogen compounds (67). Continuous processes give silanes (and some siloxanes) containing Si—O—C linkages in good yields (73). Properties of industrially important silanes are shown in Table 4.

Table 4. Properties of Silanes*

	Boiling	Density.	Refractive
Compound	point, °C	g/cm³	index, no
HSiCl₃	32	1.3298	1.3983
(C ₂ H ₅)SiCl ₅	100	1.2342	1.4257
(C ₂ H ₅) ₂ SiCl ₂	129	1.0472	1.4291
(C ₂ H ₅) ₃ SiCl	146	0.8977 ^r	1.4299
$(C_2H_5)SiH(C1)_2$	74.5	1.0926	1.4148°
(C ₆ H ₅)SiCl ₃	201.5	1.3185	1.5245
$(C_6H_5)_2SiCl_2$	305	1.218	1.5765 ^d
$(C_6H_5)SiH(Cl)_2$	184	1.2115	1.5257°
(CH ₂)(C ₆ H ₅)SiCl ₂	205	1.174	1.5180°
(CH ₃) ₂ (C ₆ H ₅)SiCl	193.5	1.032*	1.5082
(CH ₃)(C ₆ H ₈) ₂ SiCl	93	1.085°	1.5742°
(C ₂ H ₃)SiCl ₃	92	1.265	1.4330
(CH ₃)(C ₂ H ₃)SiCl ₂	93	1.085	1.4200
(CH ₃) ₂ (C ₂ H ₃)SiCl-	83	0.884	1.4141
(CH ₂)(CF ₂ CH ₂ CH ₂)SiCl ₂	122	1.211°	1.3817
(CNCH ₂ CH ₂)SiCl ₃	224	0.9699⁴	1.4103°
(CH ₃)(CNCH ₂ CH ₂)SiCl ₂	215	1.187	1.4564°
(CH ₃) ₂ Si(OCH ₃) ₂	80.5	0.8646°	1.3708
(CH ₃)Si(OCH ₃) ₃	103.5	0.955	1.3687
(CH ₃) ₃ Si(OCH ₃)	56.5	0.7537	1.3678°
Q			
(CH ₃)Si(OCCH ₃) ₃	95	1.1677	1.407
(CNCH ₂ CH ₂)Si(OC ₂ H ₅) ₅	224	0.978	1.4160
(NH ₂ CH ₂ CH ₂ CH ₂)Si(OC ₂ H ₅) ₃	217	0.943	1.4190
[(CH ₃) ₃ Si] ₂ NH	125.5	0.774	1.4078

[°] Refs. 19 and 20.

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Almost any functional group can be introduced into the side chain of an alkyl- or aryl-substituted silane (49). Methods include reactions of halomagnesium or lithium derivatives with chlorosilanes; halogenation of alkyl groups followed by nucleophilic substitution or dehydrohalogenation; addition of silicon hydrides to olefins containing polar substituents, eg, epoxyalkylsilanes from allyl glycidyl ether and similar vinylepoxy compounds; substitution on the aromatic rings of arylsilanes; hydrolysis, aminolysis, transesterification, or reduction of cyanoalkylsilanes, carboxyalkylsilanes, or carboxylic ester-substituted alkylsilanes (to obtain acids, alcohols, amines, amides, etc.); additions to multiple bonds attached to silicon; and acetoacetic ester and malonic ester syntheses (19,20, 35,36,67,74).

^b At 25°C unless otherwise noted.

^{*} At 20°C.

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The reactions of silanes with side chains bearing functional groups can usually be predicted from the known chemistry of the functional group and of the silane function. However, the chemistry may change when such groups are α or β to silicon. Functional groups generally behave normally when separated by three or more carbon atoms from silicon. Thus, under conditions for nucleophilic substitution, chloromethyl might undergo competitive cleavage, 2-chloroethyl is prone to cleavage, and 3-chloropropyl substitutes as expected. In the reaction of ammonia with a 3-chloropropyl group, 3-chloropropyltrichlorosilane cannot be used because the reaction of Si—Cl with NH₃ is favored. 3-Chloropropyltrimethoxysilane, on the other hand, gives a reasonable yield of the desired 3-aminopropyl compound (19). Such nucleophilic substitutions can also be used to prepare mercaptan and sulfide derivatives (67).

Carbon-functional silanes hydrolyze to polymeric siloxanes in which the second functional group, eg, the halogen, ester, amide, nitrile, sulfide, mercaptan, or carboxylic acid, contributes secondary polyfunctionality and most commonly serves as the means of cross-linking or introducing polar groups that can later be used to obtain desirable properties (67).

Chlorosilane Reactivity

Chlorosilanes are reactive toward polar reagents. The first step leads to the replacement of one or more halogens, usually by an attacking nucleophile.

$$RSiCI + HOH \longrightarrow RSiOH + HCI$$

$$RSiCI + C_2H_5OH \longrightarrow RSiOC_2H_5 + HCI$$

$$RSiCI + C_6H_5OH \longrightarrow RSiOC_6H_5 + HCI$$

$$RSiCI + CH_3COOH \longrightarrow RSiOOCCH_2 + HCI$$

$$RSiCI + 2 R'NH_2 \longrightarrow RSINHR' + R'NH_3CI$$

Such reactions provide a number of intermediates that can serve as starting materials for polymer synthesis. Silanols, alkoxy- and aroxysilanes, acyloxysilanes, silylamines, and related products with functional substituents can all be converted to polymers, usually under milder conditions than halogen-substituted silanes. The complex nature of these organosilane reaction pathways, implied in the production of mixtures rather than individual compounds, poses many problems in identification and separation, but also makes possible an unusual versatility in subsequent processing and ultimate applications.

To understand substituent effects in silicone chemistry, the inherent dif-

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ferences (as well as the similarities) between carbon and silicon and the differences between a carbon-carbon and a silicon-oxygen polymer backbone must be considered. Factors that account for substituent effects in silicones include electronic character (inductive and resonance), bulk steric effects, bond covalency, bond angles, the ability of silicon to expand its covalency, and π-bonding effects.

The most reactive organochlorosilanes are the methylchlorosilanes, in which low steric bulk facilitates reactivity, especially toward nucleophilic substitution. Substitution of more electronegative groups for methyl (such as ClCH₂) increases the reactivity even further, as measured, for example, by hydrolysis equilibrium constants (75).

The higher alkylchlorosilanes are far less reactive, mainly because of steric inhibition and the effect of enhanced electron release. In branched chain alkylsilanes, eg, t-butylchlorosilanes, greater steric inhibition and electron release reduce the reactivity toward nucleophilic substitution and in condensation reactions. Similarly, bis-t-butylsilanediol is extremely stable in contrast to dimethylsilanediol, which is difficult to prepare and keep in pure form.

The phenylchlorosilanes are much less reactive than methylchlorosilanes. The bulkiness of the phenyl group more than offsets its electron-withdrawing power. Triphenylchlorosilane and other triarylchlorosilanes are insoluble as well as unreactive. Ring-substituted phenylchlorosilanes exhibit the usual electronic effects of substituents in the aromatic ring. Electron-releasing substituents enhance nucleophilic substitution, whereas electron-withdrawing groups produce the opposite effect.

In certain cases π -bonding effects are observed. Such groups as "NO₂, (CH₃)₃P⁺, and 'P(OC₂H₅)₂, particularly when attached in the para position, influ-

ence reactivity because of $d\pi$ - $p\pi$ bonding (19,20,35,36,67).

Hydrolysis of Reactive Organosilicon Compounds

The silicone oligomers and polymers are formed by reaction between an organohalogenosilane or other reactive organosilane and water.

$$n X - Si - X + n H_2O \longrightarrow -Si - O_{3n} + 2n HX$$

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where X may be a halogen or any other hydrolyzable group and R and R' may be alkyl or aryl groups or other hydrolyzable groups. In the latter case further reactions leading to cross-linking can occur. When X is a halogen, this reaction is normally heterogeneous, highly exothermic, and difficult to control. Mechanistically, it probably never conforms to this simplified equation. The process can be modified and controlled.

The transformation of an organochlorosilane to a polysiloxane takes place in a series of complex steps. To arrive only at the dimer stage, all of the reactions given below are possible in a freely reacting system:

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In other words, it may be assumed that every chlorosilane can react with water; every chlorosilane can react with any silanol; every silanol can condense with any other silanol; and most steps are reversible (in theory, but not always in practice). When hydrolysis takes place in the presence of a reactive solvent, such as an alcohol, carboxylic acid, or anhydride, alkoxy or acyloxy derivatives are formed, and these react further:

$$-\stackrel{|}{\text{SiCl}} + \text{ROH} = -\stackrel{|}{\text{SiOR}} + \text{HCl}$$

$$-\stackrel{|}{\text{SiCl}} + \text{RCOOH} = -\stackrel{|}{\text{SiOOCR}} + \text{HCl}$$

$$-\stackrel{|}{\text{SiOR}} + -\stackrel{|}{\text{SiCl}} - -\stackrel{|}{\text{SiOSi}} + \text{RCl}$$



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$$-\frac{1}{5}iOR : -\frac{1}{5}iOH = -\frac{1}{5}iOS_{1} - ROH$$

$$-\frac{1}{5}iOR - HCI - -\frac{1}{5}iOH - RCI$$

$$-\frac{1}{5}iOOCR - -\frac{1}{5}iOH = -\frac{1}{5}iOS_{1} - HOOCR. etc$$

Heat of Reaction and Free Energy. For the equilibrium, 2 $R_3SiCl + H_2O = (R_3Si)_2O + 2$ HCl, the heat of reaction is approximately -100 kJ/mol (-24 kcal/mol) when $R = CH_3$. The free energy of the hydrolysis reaction is highly sensitive to the nature of the organic substituents, varying from -65.7 kJ/mol (-15.7 kcal/mol) for (C_2H_5) $_3SiCl$ to -81.2 kJ/mol (-19.4 kcal/mol) for ClCH $_2Si(CH_3)_2Cl$ at $25^{\circ}C$ (75). The hydrolysis equilibrium constants for the same chlorosilanes vary from 3.5×10^{-11} to 1.8×10^{-8} . These wide variations are due to the inductive effects of the organic substituents attached to silicon.

Oligomeric Hydrolysis Products. α,ω -Dichlorooligosiloxanes can be isolated from hydrolysates of dialkyldichlorosilanes, especially in the presence of polar solvents; examples are as follows: $\text{Cl}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_2\text{Cl}\ (n=1-4);$ $\text{Cl}[\text{Si}(\text{C}_2\text{H}_5)_2\text{O}]_n\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}\ (n=1-3);$ and $\text{Cl}[\text{Si}(\text{C}_6\text{H}_5)_2\text{O}]_n\text{Si}(\text{C}_6\text{H}_5)_2\text{Cl}\ (n=1-3)$ (76–78). Oligomers are more easily isolated from diorganodialkoxysilanes, especially if only catalytic amounts of acid or alkali are used in the hydrolysis (79,80). Careful hydrolysis of α,ω -dichloropolysiloxanes gives the corresponding α,ω -diols (81,82).

The hydrolysis of organotrihalogenosilanes follows a similar course, but is much more complex because of the larger number of possible reaction paths. A partial reaction scheme would include the steps shown below.

$$RSiCl_3 - H_2O \xrightarrow{-HCl} RSiCl_2OH \xrightarrow{H_2O} RSiCl_1OH)_2 \xrightarrow{H_2O} RSi(OH)_3$$

$$RSiCl_3 + RSiCl_2OH \longrightarrow RSiCl_2OSiCl_2R + HCl$$

$$RSiCl_3 + RSiCl(OH)_2 \longrightarrow RSiCl_2OSiCl(OH)R + HCl$$

$$RSiCl_2OSiCl_2R + RSiCl_2OH \longrightarrow RSiCl_2OSi(R)CIOSiCl_2R + HCl$$

$$RSiCl_2OSi(R)CIOSiCl_2R + RSiCl_2(OH) \longrightarrow RSiCl_2OSi(R)OSiCl_2R + HCl$$

$$RSiCl_2OSi(R)CIOSiCl_2R + RSiCl_2(OH) \longrightarrow RSiCl_2OSi(R)OSiCl_2R + HCl$$

$$OSiCl_2R$$

$$RSiCl_2OSi(R)CIOSiCl_2R + RSiCl(OH)_2 \xrightarrow{-HCl} RSiCl_2OSi(R)CIOSI(R)CI$$

(RSiClO)4 (cyclic tetrasilexane) etc

Tertiary amines used as acid acceptors stabilize some of these intermediate products. The hydrolysis of organotrialkoxysilanes is easier to control than that of the halogenosilanes, and both linear and cyclic oligomers can be isolated (83–87).

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More complex cyclic products are also formed; many of these can be isolated under favorable circumstances (88).

Silsesquioxanes. The hypothetical monomer unit RSiO_{1.5},

is formally analogous to the equally hypothetical sesquicarboxylic anhydride R(C2O3)1.5. However, although oligomers of tricarboxylic anhydrides of empirical composition RC₃O_{4.5} have scarcely ever been recognized, many interesting oligomers of empirical composition RSiO1.5 are known. The low molecular weight, crystallographically cubic, polycyclic octamers (C2H5SiO1.5)8, (n-C3H7SiO1.5)8, $(n-C_4H_9SiO_{1.5})_8$, and $(C_6H_{11}SiO_{1.5})_8$ and a cyclic dodecamer $(CH_3SiO_{1.5})_{12}$ are produced by heating oily polymers obtained on hydrolysis of organotrichlorosilanes with strong alkalies (89). The high melting crystalline octamer ($\mathrm{CH_3SiO_{1.5}}$)8 sublimes in a high vacuum above 400°C. The octamers (n-C5H11SiO1.5)8 and (C₆H₅SiO_{1.5})₈ are obtained in reasonable yields on hydrolysis of n-C₅H₁₁Si(OC₂H₅)₃ and C₆H₅Si(OC₂H₅)₃ (85). The parent octameric silsesquioxane (HSiO_{1.5})₈ and higher oligomers have also been reported (90,91). Lower melting, more readily sublimable hexamers, eg, $(CH_3SiO_{1.5})_6$ and $(C_2H_5SiO_{1.5})_6$, have been characterized (88), and two tetrameric silsesquioxanes, (i-C3H7SiO1.5)4 and (t-C4H9SiO1.5)4, have been reported (92).

The known crystalline oligomeric silsesquioxanes may be visualized as composed of fused tetracyclosiloxane rings as shown below.

$$\begin{array}{c} \begin{pmatrix} R & R \\ I & I \\ Si - O - Si - O \\ O & O \\ I & I \\ Si - O - Si - O \\ R & R \end{pmatrix}$$

When n = 2, tetragonal symmetry is indicated. When n = 3 or 4, hexagonal or octagonal symmetry, respectively, is expected. Crystallographic relations are less clear-cut in the known decamers and dodecamers.

The rough geometry that prevails in the low molecular weight cyclic silsesquioxanes is shown in the structures in Figure 4. The eight-membered ring segments are depicted by squares, but the presence of oxygen between each pair of silicon atoms is to be assumed, as is an alkyl or aryl substituent at each corner silicon atom (as suggested by the CH₃—Si in the first structure).

The oligomeric organosilsesquioxanes (RSiO_{1.5})_n can be prepared by basecatalyzed siloxane rearrangements of hydrolysates of organotrichlorosilanes or their derivatives. The solvent for hydrolysis is important because it favors cyclization and silanol retention. Such hydrolysates contain oligomers and lower molecular weight polymers that are built of cagelike units. The residual silanol content can be as high as 10%. Heat converts these polymers to infusible resins or gels. Gently removing the solvent, however, yields a viscous liquid or soluble

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Fig. 4. Geometry for low molecular weight silsesquioxanes.

solid. Oligomeric silsesquioxanes are formed in good yields if these hydrolysis products are heated with alkali. The base-catalyzed rearrangement of methyltriethoxysilane hydrolysates produces a homologous series of low molecular weight crystalline methylsilsesquioxanes (89,93–95).

Without special care the hydrolysis of organotrichlorosilanes is typically vigorous. Conversion of Si—Cl to Si—OH is rapid, and condensation results in a complex, irregular, highly cross-linked, insoluble polymer. The organosilses-quioxane oligomers can be considered as prototypes of these resins only because their functionality is closed through intramolecular silanol condensation. Mere traces of the organosilsesquioxane oligomers can be obtained by heating such resins over 200°C, for example (89).

At one time it was thought that phenylsilsesquioxane could be equilibrated at high concentrations to form soluble high molecular weight polymers, termed ladder polymers because of the structure assigned to them (96). It is now recognized that these compositions were not true equilibrium compositions. They were most likely of an intermediate form in which polycyclic structures akin to those of organosilsesquioxane oligomers are linked together by open functionality. Ultimately, equilibration of $C_6H_5SiO_{1.5}$ at high concentrations does not give a soluble product (97).

The hydrolysis, condensation, and equilibration phenomena that occur in these T systems can provide clues to the mechanisms and structures in various DT, MQ, and MDQ systems encountered in silicone resin technology.

Silanois. An understanding of the nature of the silanoi function has been of great importance in the development of silicone technology. In the early Kipping research some arylsilanois with moderate stability were isolated. They condensed to form siloxanes much more readily than the analogous carbinols. Among the methyl-substituted silicon compounds, the simplest silanois were unstable. Trimethylsilanoi, (CH₃)₃SiOH, was isolated, but was stable only when dry and free of traces of polar impurities. Dimethylsilanediol, (CH₃)₂Si(OH)₂, was isolated later (98,99). Methylsilanetriol has not yet been isolated in pure form.

Silanol groups are present in varying concentrations at various stages of the condensation of silicones, particularly in arylsilicone resins and alkylarylsilicone coreactants, and less in methylsilicone resins. The silanol function is 226 SILICONES Vol. 15

used to control physical and chemical properties and the cure rates of silicone resins and other silicone compositions.

The physical properties of silanols are similar to those of analogous carbinols. They are, for example, associated in the liquid state, presumably through hydrogen bonding (100). Ir studies indicate that silanols are much more acidic than related carbinols, but only slightly less basic (101).

Silanemonols. Most simple silanols lose water on distillation or melting, or sometimes at room temperature, to give the disiloxane. The parent silanol H_3SiOH apparently has not been isolated, nor have the simplest monoalkylsilanols. Dialkylsilanols and diarylsilanols have been prepared, eg, diethylsilanol, $(C_2H_5)_2Si(H)OH$.

Silanols are stabilized by the presence of bulky substituents. A methyl group is of insufficient bulk, and trimethylsilanol is consequently difficult to obtain free of the disiloxane. Triethylsilanol is much more stable and readily obtained pure; higher trialkylsilanols are even more stable. Triphenylsilanol is not easily converted to the disiloxane, whereas tri-1-naphthylsilanol is stable to both alcoholic KOH and acids.

Silanediols. The parent silanediol $H_2Si(OH)_2$ (102) is stable only for a few minutes. Methylsilanediol, $CH_3SiH(OH)_2$, and ethylsilanediol, $C_2H_5SiH(OH)_2$, apparently have not been isolated, and even dimethylsilanediol eluded investigators for many years. Dialkylsilanediols with bulky substituents are increasingly stable, eg, di-n-propylsilanediol, di-n-butylsilanediol, diisopropylsilanediol, diisobutylsilanediol, and dicyclohexylsilanediol. Di-t-butylsilanediol is rather difficult to dehydrate. Diethylsilanediol is soluble in water up to 5 g/100 g at 0° C and 16 g/100 g at 40° C (19).

The alkylarylsilanediols are stable as a class, and several were prepared during the early Kipping research. Alkylphenyl- and alkylnaphthylsilanediols are readily prepared by hydrolysis of the corresponding diacetoxysilanes. Diarylsilanediols are quite easy to prepare and are among the most stable of the silanediols.

Polysiloxanediols. Synthesis of the lower members of this class is difficult, and careful control of pH and temperature is necessary to prepare tetramethyldisiloxanediol, $(CH_3)_2Si(OH)$ —O— $Si(OH)(CH_3)_2$. The diphenylsiloxanediol oligomers $HO[(C_6H_5)_2SiO)]_nH$ (n=2,3,4) were obtained by Kipping; many other disiloxanediols have been prepared since (76,81).

Silanetriols. Phenylsilanetriol was prepared (103) from phenyltrimethoxysilane and dilute acetic acid at ca 10°C. Others, such as dichlorophenylsilanetriol (104) and cyclohexylsilanetriol (95), have since been prepared. Phenylsilanetriol is slightly soluble in water (19).

Silanetetrol. Monosilicic acid has been prepared only in solution and is stable only within a very narrow pH range.

Disiloxanetetrols. Disiloxanetetrols have been obtained by partial hydrolysis of triacetoxysilanes under mild conditions. Examples are 1,3-diphenyldisiloxanetetrol, bis(dichlorophenyl)disiloxanetetrol, and 1,3-dicyclohexyldisiloxanetetrol (105,106).

Cyclotetrasiloxanetetrols. Tetraphenyl and tetracyclohexylcyclotetrasiloxanetetrols can be obtained by careful hydrolysis of the organotrichlorosilanes in dilute solutions (107).

Reactions. Most reactions by which silanols are prepared, as described

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above, are reversible, giving halogenosilanes, acyloxysilanes, alkoxysilanes, silylamines, and others. Alkali silanolates can be obtained from certain silanols by treatment with the alkali amide or with concentrated alkali metal hydroxides.

In the acid- or base-catalyzed reaction with alcohols, under nonequilibrium conditions, self-condensation of the silanol and alcoholysis of the resulting disiloxane are competing reactions (108). Inductive effects of substituents strongly affect rates in either case. Inductive and resonance effects are also observed in the thermal self-condensation of silanols (109). Aromatic silanediols condense to siloxanes at measurable rates around 200°C (110,111), frequently accompanied by Si—C bond rupture. Acidic catalysts facilitate the rupture of the Si—C bond, which leads to cross-linking during polymerization; cross-linking must be minimized in practice.

In the base-catalyzed condensation of (chloromethyl)methylsilanediol, the initial rate is given by

$$-\frac{d[SiOH]}{dt} = k_B(B)[SiOH]^2$$

With a triethylamine catalyst, electron-withdrawing groups promote the reaction, reducing the effects of steric inhibition. In acid media, on the other hand, electron withdrawal and steric effects reduce the rate (112,113).

Functionality

The role of functionality in silicone chemistry can be illustrated by the hydrolysis of methylchlorosilanes.

Monofunctional reactants can be condensed only to disiloxanes.

(CH₃)₂SiCl
$$\xrightarrow{\text{H}_2\text{O}}$$
 (CH₃)₂SiOH $\xrightarrow{\text{condensation}}$ (CH₃)₂SiOSi(CH₃)₃

Difunctional reactants are converted through chlorosilanes or silanediols to linear polymers with reactive end groups or to monocyclic compounds.

$$(CH_3)_2SiCl_2 \xrightarrow{H_2O} (CH_3)_2Si \xrightarrow{Condensation} Cl(Si(CH_3)_2O]_nH \qquad or \qquad HO[Si(CH_3)_2O]_nH$$

$$OH \xrightarrow{Condensation} -HCi \xrightarrow{C(CH_3)_2SiO]_n} OH$$

Trifunctional reactants can form dichlorosilanols, chlorosilanediols, or silanetriols, and these, upon subsequent condensation, give highly cross-linked gels (exceptions noted earlier); many reaction paths are available to trifunctional silanes.

CH₃SiCl₃
$$\xrightarrow{\text{H}_3\text{O}}$$
 CH₃SiCl₂(OH) $\xrightarrow{\text{H}_3\text{O}}$ CH₃SiCl(OH)₂ $\xrightarrow{\text{H}_3\text{O}}$ CH₃Si(OH)₃ $\xrightarrow{\text{CH}_3}$ CH₃ CH₃ $\xrightarrow{\text{CH}_3}$ CH₃Si CH₃ $\xrightarrow{\text{CH}_3}$ CH₃ CH₃ CH₃ $\xrightarrow{\text{CH}_3}$ CH₃ CH₃ CH₃ $\xrightarrow{\text{CH}_3}$ CH₃ CH₃ CH₃ $\xrightarrow{\text{CH}_3}$ CH₃ CH₃ CH₃ CH₃ CH₃ $\xrightarrow{\text{CH}_3}$ CH₃ CH₃

Tetrafunctional reactants give highly complex, usually highly hydrated, gel structures.

The characteristics and composition of end products can be controlled and modified in various ways. Chain lengths can be shortened and average molecular weights controlled by addition of small amounts of monofunctional reagents to difunctional reactants. Cross-linking can be controlled by addition of proper amounts of tri- or tetrafunctional reactants to difunctional reactants. Gelation can be retarded or prevented by adding appropriate amounts of monofunctional reactants to a system with an average functionality well above 2.0. Solubility of a polymerizing system with an average reactant functionality above 2.0 can be maintained by adjusting concentration and solvent polarity; cure can be affected by physical changes that allow further chemical reactions, usually rearrangement and cross-linking.

The hydrolysis of difunctional reactants gives a mixture of siloxanes of moderate average molecular weight with the properties of a fluid. The mixture contains both linear and cyclic oligomers. Higher average molecular weight materials, ie, more viscous fluids and gums, are prepared by polymerizing purified lower cyclic compounds (mainly the n=4 oligomer), which can be distilled from the mixture. This ring-opening polymerization of cyclosiloxanes is actually a redistribution- or equilibration-type polymerization. When equilibrium is reached, there is usually a Gaussian distribution of molecular weights among the chain molecules and a decreasing distribution of cyclic oligomers with increasing molecular weight (114).

Polyorganosiloxanes with silicate structures have been prepared from inorganic mineral silicates by using a trimethylsilylation process (115). The silicate materials are treated with a mixture of HCl, i-C₃H₇OH, water, and hexamethyldisiloxane (MM). The silicate anions are converted to trimethylsilyl derivatives. Residual hydroxyl (silanol) contents allow further reactions and bodying or curing to higher molecular weight compositions (116).

Organofunctionality in silicon compounds and siloxane systems makes it possible to design formulations that contain reactive groups, which later undergo further reactions effecting cross-linking and curing. Common examples include hydrosilation,

and silanol condensation.



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Hydrolysis reactions can be the basis of cures triggered by atmospheric moisture. Acyloxy and alkoxy functionality are the most frequently employed.

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Such reactions can be controlled and may be suitable for fluid, resin, and elastomer formulations. Alkoxysilane hydrolysis is slower than acyloxysilane hydrolysis.

Silicon compounds substituted with unsaturated organic groups are polymerized by free-radical, cationic, anionic, or coordination techniques, even if the silicon bears no other reactive group. Therefore, vinyl, allyl, and diene polymerization can be applied to silicone systems.

Reactive groups in siloxane polymer systems can also be used for subsequent modifications. For example, Si—H addition to unsaturated esters gives ester-functional silicones (117); the reaction of \equiv SiCH₂CH₂CH₂NH₂ with isocyana-toacrylates gives acrylofunctional silicones (118). Silicone-organic block copolymers can also be made in this fashion.

Silphenylenes. Attempts to build chain stiffness into polysiloxanes centered on silphenylenes. The common methylsilicone and methylphenylsilicone elastomers were soft, flexible materials of low crystallinity, with low glass-transition temperatures and poor solvent resistance. The introduction of stiff aryl segments in the main chain between siloxane units was expected to improve these properties and increase thermal and oxidative stability.

Even simple disilphenylenes cannot be prepared by direct methods (except in insignificant yields). Using diffunctional Grignard reagent or its equivalent, 1,4-dilithiobenzene produces other substitution products simultaneously and the usual separation problems are encountered.

Better yields are obtained by starting from alkoxychlorosilanes. Yields are also improved by using dimethylchlorosilane, (CH₃)₂SiHCl, and preparing the Grignard reagent in ether in its presence. The disilphenylene dihydride is converted to the dialkoxy derivative and then to the diol (119).

Silphenylenes are also prepared by hot-tube reactions from benzene and dimethyldichlorosilane or methylphenyldichlorosilane.

$$+ 2 (CH_3)_2 SiCl_2 \longrightarrow CIS_i \longrightarrow CH_3$$

$$CH_3 \longrightarrow CH_3$$

$$CH_3 \longrightarrow CH_3$$

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} CH_3 \\ CH_3 \end{array} \\ + \ 2 \ CH_3 (C_6H_6)SiCl_2 \end{array} \longrightarrow \begin{array}{c} CH_3 \\ CISi \\ C_6H_5 \end{array} \begin{array}{c} CH_3 \\ SiCl + 2 \ HCl \end{array}$$

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Silyl-substituted aryl halides and silyl hydrides give silphenylenes in moderate yields above 500°C.

$$Cl - \underbrace{\hspace{1cm} SiR_3 - HSiR_1^2 \frac{hot}{tube} \ HCl - R[Si - \underbrace{\hspace{1cm} SiR_1} - SiR_1]}_{}$$

Silicone polymers with the repeating unit

exhibit the increased crystallinity and chain stiffness conferred by the arylene chain segments (119-121).

Polysilanes. In polysilanes the polymer chain consists entirely of silicon atoms (27,122,123). Such materials were probably made by Kipping in the 1920s, but were first described about 20 years later. More recent work (122,123) has expanded the understanding of polysilane synthesis and properties and pointed to potential technological applications (see also POLYSILANES AND POLYCARBO-SILANES.

Polysilanes are made from diorganodichlorosilanes by treatment with sodium metal in a hydrocarbon diluent above 100°C.

A wide variety of substituents is possible; R can be hydrogen (with care) or alkyl or aryl groups. The R groups on the starting chlorosilane can be different, and mixtures of different chlorosilanes can be used for the reaction. The mechanism is complex and not yet clear. Measured molecular weights seem to be high.

The properties of polysilanes depend on the organic groups attached. Thus $[(CH_3)_2Si]_n$ is highly crystalline and insoluble; $[(CH_3)(n-C_3H_7)Si]_n$ is a soluble solid; and $[(CH_3)(n-C_6H_{13})Si]_n$ is an elastomeric rubbery material. Aryl groups raise the softening point of the polymer.

Polysilanes are electrical insulators, but become semiconducting when treated with SbF₅ or AsF₅. Cross-linking can lead to ceramic applications. The introduction of silacyclopentane rings, when opened oxidatively, gives evidence for Si—O—Si and Si—O—C bonds. Compositions analogous to room-temperature vulcanized (RTV) materials are suggested by chemical cross-linking by polysilane Si—H with a trialkenylsilane. Thermal and photochemical cross-linking involves free radicals.

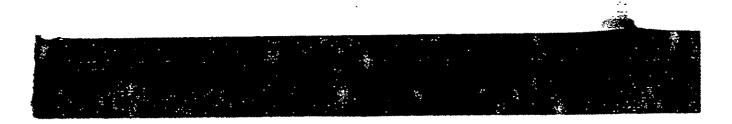
Possible industrial uses include silicon carbide production from polysilane precursors, photoresists, and photoinitiators.

Metallosiloxanes. Metallosiloxanes may be defined as condensation products of organosilanes and di- or polyvalent metal-oxygen compounds in which the backbone structure consists of —Si—O— and —M—O— bonds arranged in various sequences. Stannosiloxanes and titanosiloxanes are relevant to the present discussion because of the catalytic activity of the metals in silicone systems. Other metallosiloxanes investigated include those with arsenic, boron, aluminum, germanium, zirconium, and phosphorus (83,124–132).



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Stannosiloxanes. Hydrolysis of a mixture of organochlorosilanes and organochlorostannanes, followed by heating of the hydrolysates, produces polymers with Sn-O-Si backbones; the Sn-O portion of the chain is almost invariably smaller than the stoichiometry of the reaction would require. Disproportionation apparently occurs with the loss of volatile organotin compounds. Certain low molecular weight Sn-O-Si compounds, eg, [(CH₃)₃SiO]₂Sn(CH₃)₂, are useful as lubricant additives (133).

Hydrolysis of a mixture of chlorosilanes and chlorostannanes gives a mixture of oligomeric stannosiloxanes (134). Other preparative methods for oligomers and low molecular weight polymers include the reaction of chlorostannanes with silanolates in benzene or similar inert solvent, the condensation of alkoxysilanes with acetoxystannanes in the presence of reesterification catalysts, and the reaction of silanols with alkylchlorostannanes in the presence of ammonia or an amine (135-138).

Titanosiloxanes. Titanosiloxanes contain tetravalent titanium, and since the Ti-C bond is unstable, the titanium compound is also tetrafunctional. Thus titanium tetrachloride and ethyl orthotitanate are the preferred starting materials. Many compounds have been prepared by the methods used for Sn-O-Si and other systems (139-141).

Titanosiloxane polymers are prepared (142,143) by the reaction of polysiloxanediols and TiCl4; heating converts the product to higher molecular weight polymers with glass-transition temperatures of ca - 100°C. They are amorphous at 20°C, but show considerable crystallinity at lower temperatures. Different polymers are obtained by the reaction between the hydrolysis products of alkyltrichlorosilanes, aqueous alkali, and TiCl4, followed by heating. These polymers are hard, brittle, glassy materials, which are soluble in organic solvents, but melt above 500°C; heating to ca 400°C confers insolubility.

To prepare linear polymers, two valencies of the titanium can first be employed in siloxane substitution to obtain a difunctional intermediate, which polymerizes by an elimination reaction.

Soluble, film-forming, and fiber-forming polymers in the molecular weight range of 104-105 have been reported. Introduction of siloxanes into the backbone gives linear polymers (144).

where R' and R" are CH_3 or C_6H_5 and n may be 50-100.

Partial hydrolysis of tetrakis(trialkylsiloxy)titanium compounds gives low molecular weight polymers, which disproportionate upon heating to produce higher molecular weight polymers of complex structure (131).

Titanium, with a maximum covalency of six, forms chelates with such lig-

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ands as 8-hydroxyquinoline. A typical model compound with Ti-O-Si bonds is formed by reaction with a silyl ester.

$$C_3H_2O - T_1 - OC_3H_1 + 2 C_6H_4 CH_4 CH_4 CH_5 SIOOCCH_3$$

$$C_8H_5(CH_3)_2SiO - T_1 - OSi(CH_3)_2C_6H_5 + 2 C_3H_2OOCCH_3$$

Chelated titanosiloxane polymers are formed similarly with di- or trifunctional silanes (145,146).

$$\bigcap_{N} \bigcap_{N} \bigcap_{C_6 H_5} \bigcap_{j_2 \text{Si}(OOCCH_3 I_2} \bigcap_{j_2} \bigcap_{C_6 H_5} \bigcap_{C_6$$

Uses

Silane chemicals are being used as silylation agents in synthetic and analytical chemistry (147). A number of effective reagents developed for the preparation of alkoxy- and aroxysilanes by silylation of alcohols and phenols can also be used to silylate amines and other compounds containing reactive hydrogen. Trimethylsilylation often provides a convenient method for the purification of phenols, polyols, sugars, amino alcohols, amino acids, steroids, peptides, and other compounds that are difficult to separate or purify by other means. Trimethylchlorosilane (in the presence of ammonia or an amine as acid acceptor), hexamethyldisilazane, a mixture of trimethylchlorosilane and hexamethyltrisilazane, alkyltrimethylsilylamines, N-trimethylsilylamides, and bis(trimethylsilyl)acetamide are used (148–155); silylamines are particularly useful (156,157).

Silylation is also used for the manufacture of drugs. The enzymatic techniques for making 6-aminopenicillanic acid from Penicillin G or V can be replaced

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by a process using methylchlorosilanes as blocking agents for the treactive) carboxylic acid moiety. This silylation process is now widely used (6).

Other applications include the use of moisture-reactive silanes as dehydration agents (158.159) and Si—H compounds as reducing agents (160,161). Certain organosilanes, eg. chloromethyltrimethylsilane, are particularly useful for synthetic transformations in organic chemistry; chloromethyltrimethylsilane is made by the photochlorination of tetramethylsilane (162).

Copolymerization of silane monomers with appropriate organic monomers gives random silicone-organic copolymers, such as silicone-polyimides; they can be formulated to combine the desirable features of silicones with those of organic polymers. In addition to providing tough films that adhere to many substrates, these compositions have excellent release properties, resist deformation at elevated temperatures, have good corona resistance, and protect substrates from corrosion (163,164).

Polyolefins can be made moisture cross-linkable by melt grafting with hydrolyzable organosilanes such as alkenyl-functional trialkoxy- or triacyloxysilanes; grafting is easily done in an extruder with a peroxide initiator. The grafted polyolefin is formed into the shape of the desired article and cross-linked above 80°C in the presence of water. This process is used for wire and cable insulation 165).

The most important application of reactive silanes is the formation of silicone films. The silane can be applied directly, deposited from solution, or deposited as a vapor. In such applications silanes are preferable to siloxane compositions for various reasons, including the thinness of the desired film and the shape of the substrate. In in situ film formation some silane reactivity remains for surface attachment. Such a silicone coating can be used to waterproof a fabric, protect electrical parts, prevent siliceous powders from caking, and improve the bondability of surfaces (166).

Silane coupling agents (167,168), when properly applied to the surfaces of inorganic materials, markedly enhance their compatibility with organic polymers. Strength properties of mineral-reinforced plastics are increased by silane coupling agents deposited to form adsorbed films on the filler surface, which is modified according to the functional nature of the silanes. 3-Aminopropyltriethoxysilane is widely used as a coupling agent with epoxy, phenolic, amide, and related plastics. It is prepared commercially by the following reactions (67):

$$Cl_{3}SiH + CH_{2} = CHCN \xrightarrow{base} Cl_{3}SiCH_{2}CH_{2}CN$$

$$Cl_{3}SiCH_{2}CH_{2}CN + 3 C_{2}H_{5}OH \longrightarrow (C_{2}H_{5}O)_{3}SiCH_{2}CH_{2}CN + 3 HCI$$

$$(C_{2}H_{5}O)_{3}SiCH_{2}CH_{2}CN + 2 H_{2} \xrightarrow{pressure} (C_{2}H_{5}O)_{3}SiCH_{2}CH_{2}CH_{2}CH_{2}NH_{2}$$

In a related application 3-aminopropyltriethoxysilane is employed to modify the surface of glass beads for enzyme immobilization. Trypsin, for example, can be bonded to the surface by diazonium coupling with the amino group (azo linkage). In this form it promotes biochemical reactions like protein hydrolysis. Expensive enzyme costs are reduced because easy recovery permits recycling (169).

Liquid crystal silane compounds can be chemically bonded to substrates (170). This illustrates further the unique opportunities for product development or modification through organofunctional silane chemistry.

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Silicone Polymers

Industrial uses of organosilanes include surface treatments of fillers and reinforcing components of resin and elastomeric composites (166–168), silvlation in organic synthesis (6,147), and group-transfer polymerization (171,172). However, the principal use for these organometallic intermediates is in the production of siloxanes formed by hydrolyses and condensations starting with chlorosilanes or alkoxysilanes. Nonhydrolytic processes (67) are used only in the synthesis of specialty materials.

The three commercially important classes of silicone polymers include silicone homopolymers, silicone random copolymers, and silicone-organic (block) copolymers. Polydimethylsiloxanes constitute by far the largest volume of homopolymers produced today (173).

PDMS is usually the principal component of the random copolymers and the principal siloxane component of most silicone-organic copolymers. The production of commercial silicone homopolymers and random copolymers and the synthesis of siloxane intermediates for silicone-organic copolymers usually involves acid- or base-catalyzed equilibration of linear or cyclic siloxane oligomeric intermediates. These intermediates are formed during hydrolysis of difunctional silane reactants. The lower molecular weight cyclic compounds can be stripped from the hydrolysate. Cyclic compounds are also obtained by depolymerization of linear polymers, which readily crack when heated with caustic.

$$HO[(CH_3)_2SiO]_mH - \frac{KOH}{200^mC} + \{(CH_3)_2SiO\}_3 + \{(CH_3)_2SiO\}_4 + \{(CH_3)_2SiO\}_5 + \cdots + H_2O(CH_3)_2SiO\}_5 + \cdots + H_2O(CH_3)_2SiO\}_5 + \cdots + H_2O(CH_3)_2SiO\}_6 + \{(CH_3)_2SiO\}_6 + \{(CH_3)_2SiO\}_6 + \{(CH_3)_2SiO\}_6 + (CH_3)_2SiO\}_6 + (CH_3)_2SiO\}_6 + (CH_3)_2SiO\}_6 + (CH_3)_2SiO\}_7 + \cdots + H_2O(CH_3)_2SiO\}_7 + (CH_3)_2SiO\}_7 + (CH_3)_2SiO]_7 + (CH_3)_7 +$$

Cyclic tetramer is the main component obtained from base-catalyzed thermal cracking; the reaction is driven by removal of the product. Ring-opening polymerization of purified cyclic components leads to higher molecular weight materials (67,114,174).

The highest molecular weight silicone polymers (gums) are made by using strong bases such as KOH as catalysts, usually in batch processes. Large volume grades are also produced in continuous reactors (175).

Molecular weight is controlled by chain-terminating groups. The trimethylsiloxy group (100) from hexamethyldisiloxane results in polymers that do not polymerize further by chain extension.

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Reactive end groups are important in many applications. Molecular weight can also be controlled by reactive end groups such as silanol, alkoxy, vinyl, or hydrogen from the appropriate reactant. ie. water, alcohol, divinyltetramethyldisiloxane, or tetramethyldisiloxane, respectively.

Silanol and alkoxy terminated polymers can further build molecular weight by condensation reactions. Vinyl and hydrogen chain-terminated polymers can build molecular weight by catalyzed hydrosilation reactions (176) or by radiation- or peroxide-induced free-radical processes (177,178). Intermediates used in the synthesis of silicone-organic copolymers can also have other reactive end groups such as aminoalkyl (for silicone-polyimides) and chlorine (for silicone-polycarbonates) (179–181).

Hydrolysis and Equilibration. The first step in the conversion of chlorosilanes to useful polymer products is hydrolysis. The chlorosilanes are hydrolyzed to silanols, which condense rapidly to siloxanes:

When dimethyldichlorosilane is hydrolyzed with excess water, the hydrogen chloride evolved is partially or completely dissolved in the aqueous phase, and a light,

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colorless siloxane oil separates as a second phase. Both linear and cyclic polydimethylsiloxanes are formed.

Approximately half of this oil consists of a mixture of cyclic species of empirical composition $\{(CH_3)_2SiO\}_n$, mainly tetramer (n = 4).

Only a small amount of trimer (n=3) is formed. Decreasing amounts of higher membered cyclic compounds (up to n=10) can be separated and identified (182–184). The series of cyclic polysiloxanes probably extends at least to values of n equal to several hundred (184). No low molecular weight diols are found in crude dimethyldichlorosilane hydrolysates, but numerous higher molecular weight α, ω -diols are present in low concentrations.

In one such process the chlorosilane is mixed with 22 wt % azeotropic aqueous hydrochloric acid in a pump and heat-exchanger loop. The mixture of (fluid) hydrolysate and concentrated acid (32 wt % HCl) is separated in a decanter. The silicone hydrolysate is washed to remove residual acid, neutralized, dried, and filtered. The equipment is made of glass-lined steel or other acid-resistant materials (185).

Batch, continuous-loop, and vapor-phase hydrolysis processes are used on a commercial scale. The ratio of cyclic to linear polymers obtained in the direct hydrolysis of dimethyldichlorosilane depends on the hydrolysis procedure, water: silane ratio, solvents, pH, and contact time. For example, if a mutual solvent for the organochlorosilane and water (eg, a low alcohol or ketone) is used, the proportion of smaller cyclic compounds is increased. The presence of strong acids likewise favors the formation of cyclic compounds with a small number of segments. Cationic surfactants increase the yield of cyclic structures (186). Low temperature or hydrolysis in the presence of water-insoluble, nonpolar solvent minimizes the formation of higher polysiloxanes. The silanols are stabilized in neutral or nearly neutral solutions and readily condense to siloxanes in the presence of strong acid or base.

Higher alkyl homologues of dimethyldichlorosilane and their substituted alkyl derivatives give higher yields of smaller cyclic compounds under comparable conditions. Diethyldichlorosilane, for example, gives 30—40% of both the cyclic trimer and tetramer when hydrolyzed in ether and over 60% of the cyclic tetramer in aqueous methanol. Even higher homologues give good yields of silanediols since steric hindrance prevents these from condensing readily to cyclic compounds



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or to higher diols. Aryldichlorosilanes also give high yields of diols, as seen earlier in the case of Kipping's work with diphenylsilanediol.

Solvent dilution or the use of polar solvents tends to stabilize the silanols. The stability of water-soluble silanols depends mainly on the pH, and different silanols are most stable at different pH. For example, trimethylsilanol is most stable at pH 7-8, dimethylsilanediol at pH 6.5, and methylsilanetriol at ca pH 4. Silanetetrol (orthosilicic acid) is stable in solution at pH 1. Many silanol-terminated oligomers, such as in the structure shown below, are fairly stable at neutral pH or slightly higher.

mpirical

Hydrolysis of a mixture of dimethyldichlorosilane and trimethylchlorosilane gives a series of trimethylsiloxy chain-terminated products along with hexamethyldisiloxane and polydimethylsiloxanes. The particular statistical distribution of the three product types

MM [(CH₃)₃Si]₂O

 $D_n = [(CH_3)_2SiO]_n$

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stituted parable e cyclic stramer inediols spounds depends on the ratios of reactants and the temperature. This distribution reflects various equilibria among the components. Furthermore, the hydrochloric acid formed enters into various equilibria and also functions as an equilibration catalyst.

This kind of equilibration of siloxanes has an important role in silicone chemistry. It is often applied for the production of polymers that do not condense further. The properties of these polymers can be varied within wide limits by an appropriate choice of substituents on the mono- and difunctional chlorosilanes. Neutralization and devolatilization of the equilibrium mixture give fluids with specific viscosities determined by the ratio of M and D groups.

Equilibration is more readily understood in systems initially containing only pure siloxanes and catalyst. The first such system studied was a mixture of hexamethyldisiloxane (MM), octamethylcyclotetrasiloxane (D_4), and sulfuric acid (187).

$$MM + D_4 \xrightarrow{H_2SO_*} MD_zM + D_z$$

This reaction involves numerous equilibria. In the equilibrium

$$MD_xM + MD_yM \Longrightarrow MD_{x-\omega}M + MD_{y-\omega}M$$

the equilibrium constant is close to a theoretical value of unity, whereas in the equilibrium

$$MD_xM = MD_{x-w}M + D_w$$

the constant is 11×0.4^w , where w is ≥ 4 ; ie, no cyclic compound smaller than D_4 is obtained in meaningful quantities. Since the cyclic trimer is known, its

60a - 1

small concentration may be due to ring strain, estimated energy ca 15 kJ/mol (3.5 kcal/mol), which causes it to be very reactive. In a solvent, eg. carbon tetrachloride, the ratios of cyclic to linear compounds and of low molecular weight to high molecular weight linear compounds increase. As the ratio of M to D increases, the proportion of cyclic compounds decreases (37,67,187).

An even simpler system consists of only pure octamethylcyclotetrasiloxane and catalyst; the disiloxane can equilibrate, but not rearrange. The base-catalyzed rearrangement, which causes the cyclotetrasiloxane to be converted to high molecular weight polymer, is used to prepare the polymer stock for many silicone elastomers. Cyclosiloxane, obtained by thermally cracking linear polymers, is used to guard against unwanted chain terminators. Because of its simplicity, this rearrangement has become a model for all such siloxane rearrangements. Elaborate mechanisms have been proposed, including attack of the acid or base on silicone, probably through a pentacovalent silicon intermediate; opening of the polysiloxane ring, probably forming a silanol and a silanolate; chain propagation through these reactive species; and closure of rings, now much increased in the average degree of polymerization (174,188–192).

Acid- and base-catalyzed equilibrations of siloxane mixtures follow a similar pattern, leading to low molecular weight end products if monofunctional components, such as hexamethyldisiloxane, are present. The term equilibration is certainly appropriate, but rearrangement, redistribution, and polymerization can also be used. Study of the ring-chain equilibria of the methylsilicones and oligomer reactivities in polymerization processes shows that the type of product desired defines the choice of oligomer starting materials (187,193).

The reaction mixtures of polydimethylsiloxane homopolymers and random copolymers contain, finally, about 12–15% volatile, lower molecular weight materials, which are usually removed by vacuum stripping at elevated temperatures after neutralization of the active catalyst. When M is absent or very low, the equilibrium mixture contains ca 85 wt % linear polymers and 15 wt % cyclic polymers. The cyclic polymers, mainly tetramer, form a continuous population at least to $D_{\rm 400}$, and those larger than $D_{\rm 12}$ make up 2–3 wt % of the total polymer in silicone oils and gums. The distribution of linear polymers is random (37).

Base-catalyzed Polymerization. Strong inorganic alkalies and quaternary ammonium hydroxides and phosphonium hydroxides polymerize octamethylcy-clotetrasiloxane to a high molecular weight polymer. In a standard procedure, for instance, the tetramer is heated for about 2 h at 140°C with 0.01% KOH and cooled, the catalyst washed out or neutralized, and the polymer devolatilized. The polymer thus formed has a number-average molecular weight of about 10°C.

The effectiveness of alkali metal hydroxides as catalysts increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, which is also the order in which the degree of ionization of their salts or silanolates would be expected to increase. Silanolates are good catalysts for the polymerization of cyclic polysiloxanes. An example is the structure following, where n=3-9 (194).

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The ionic species most intimately involved in the polymerization mechanism are silanolates formed from the base initially employed.

The catalyst must be completely removed by neutralization or thorough washing. Even traces effect polymer degradation (slowly at room temperature, but rapidly at elevated temperature).

Polymer degradation is also avoided by using a "transient" catalyst, which is effective at polymerization temperatures, but destroyed by heating for a short time to higher temperatures (195–197). Examples are tetramethylammonium hydroxide and tetrabutylphosphonium hydroxide; tetra-n-butylarsonium hydroxide is effective, but less practical. Transient catalysts produce stable silicone polymers with improved resistance to hydrolytic or thermal degradation at elevated temperatures.

The base-catalyzed polymerization of cyclosiloxanes is an ionic process involving random rearrangement of Si—O bonds. Most kinetic studies are based on this assumption. The suggested ionic mechanisms may be simplified to the following equations:

$$HO[(CH_3)_2SiO]_5Si(CH_3)_2O^- + \{(CH_3)_2SiO\}_4 \xrightarrow{\frac{k_2}{k_4}} HO\{(CH_3)_2SiO\}_7Si(CH_3)_2O^-$$

$$HO((CH_3)_2SiO)_nSi(CH_3)_2O^{-} + \{(CH_3)_2SiO\}_4 \xrightarrow{k_0} HO((CH_3)_2SiO)_{n+4}Si(CH_3)_2O^{-}$$

$$HOl(CH_3)_2SiO)_nSi(CH_3)_2O^+ + K^- \longrightarrow HOl(CH_3)_2SiO)_nSi(CH_3)_2OK$$

where k_p and k_d apply to polymerization and depolymerization, respectively.

With 0.01% KOH at 152.6°C the reaction proceeds at a rate that is first order in the volume fraction of cyclic tetramer in solution (θ_o) to an equilibrium at about 94% polymer. Depolymerization (reversion) proceeds at a rate proportional to the volume fraction of polymer. The integrated form of the rate equation is

$$-kt = \ln [\theta_o - 0.06 (1 - \theta_o)]$$

The polymerization rate is also proportional to the square root of the catalyst concentration, ie,

$$k_p = A [base]^{1/2}$$

and

$$k_d = 0.06 k_p$$

The temperature dependence of the rate has also been investigated (19,191,192,194). According to a more complex rate equation (198), the overall rate of polymerization depends on the square root of the cyclic tetramer concentration.

Entropy considerations enter prominently into such ring-chain polymerizations. In the alkali-catalyzed polymerization of dimethylsiloxane cyclic oligomers, the relative rates are in the sequence $D_3 > D_4 > D_5 < D_6 < D_7 \approx D_8 \approx D_9$. This order of reactivity has been explained by the assumption that, in the attack of a silanolate ion on the silicon atom of a cyclic compound to form a

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pentacovalent silicon intermediate, the energy change is constant, but the entropy change varies with ring size (199).

Promoters, such as small amounts of certain Lewis bases, greatly increase the rate of polymerization by alkali metal hydroxides. Tetrahydrofuran, dimethyl sulfoxide, hexamethylphosphoramide, and some phosphine oxides are effective promoters. Medium effects, particularly the dielectric constant, are also important (200-202).

The change of viscosity with time during base-catalyzed siloxane equilibrations is shown in Figure 5. The early peaks and their positions are consistent with the following observed order of reactivity: $D_3 > D_4 > D_5 > MD_2M > MDM > M_2$ (174).

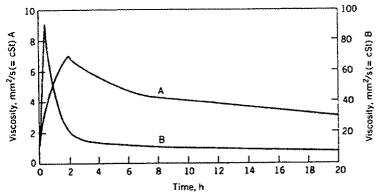


Fig. 5. Change in viscosity during equilibration of polymethylsiloxanes with tetramethylammonium hydroxide. A, M_2 and D_4 in a molar ratio of 1:1. B, M_2 and D_3 in a molar ratio of 1:1.33 (174). Courtesy of the American Chemical Society.

Acid-catalyzed Polymerization. The mechanism of acid-catalyzed polymerization of cyclosiloxanes is not well understood, despite careful investigations (191,203-208); the principal processes are cationic in nature. With protonic acids, structures of this type

$$\equiv$$
Si $-$ OH $-$ Si \equiv

most likely facilitate nucleophilic attack at silicon to effect cleavage of the Si—O bond. Sulfuric acid, for example, breaks siloxane bonds.

$$-Si-O-Si-+H_2SO_4 = -SiOH + -SiOSO_3H$$

This type of reaction provides the way for polymerization through redistribution of siloxane linkages; other mineral acids probably operate similarly (19). The idea that protonation of the oxygen in an Si—O bond initiates these polymerizations is consistent with the observed basicity of oxygen in siloxanes (209) and the order of reactivity found for siloxanes with sulfuric acid, ie, $D_3 > M_2 > MDM > MD_2M > D_4$. The change in viscosity with time during acid-catalyzed siloxane equilibrations is shown in Figure 6. The shapes of these curves follow





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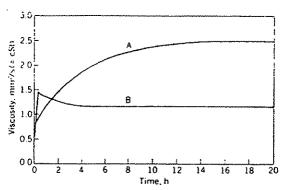


Fig. 6. Change in viscosity during equilibration of polymethylsiloxanes with sulfuric acid. A, M_2 and D_4 in a molar ratio of 1:1. B, M_2 and D_3 in a molar ratio of 1:0.55 (174). Courtesy of the American Chemical Society.

the order of reactivity with sulfuric acid (174). This behavior may be compared with that depicted for the base-catalyzed case in Figure 5.

Catalysis by both Brønsted and Lewis acids has been studied extensively. There is doubt whether Lewis acids (including hydrogen chloride) are catalysts when completely pure, dry, and not exposed to light (210). Cocatalysts such as water, carboxylic acids, or hydrogen chloride must be present in small amounts. The effective catalysts are presumably complexes such as HAlCl₄, HFeCl₄, HFeCl₃OH, or HSnCl₄OH (211,212).

A study of the kinetics of the polymerization with a tetrachloroferrate catalyst showed the rate to be first order in cyclic tetramer and second order in tetrachloroferrate. The proposed mechanism involves the reaction of a dimeric tetrachloroferrate complex with cyclic tetramer to form an intermediate such as

[HD,] - [FeCl,HFeCl,]-

which in turn reacts further with siloxanes to form other ionic intermediates similar to those for the base-catalyzed reaction. The polymerization is terminated by water to give silanol end groups, HCl to give silanol and chlorine end groups, or MM to give trimethylsiloxy end groups (211).

Copolymerization. Hydrolysis of mixtures of organochlorosilanes (or other readily hydrolyzable silanes) gives mixed siloxane products. Diorganodichlorosilanes, eg, dimethyldichlorosilane and methylvinyldichlorosilane, give low molecular weight fluids with mixed cyclic oligomers predominating. High molecular weight polymers made by hydrolysis methods are limited to those typical of silicone resins, ie, branched and cross-linked structures based on significant amounts of organotrichlorosilanes and sometimes SiCl₄.

Copolymerization of siloxanes extends the possibility of modification to provide specific properties for particular applications (14,213). In simple cases different cyclic siloxanes and catalysts are mixed, and random copolymerization occurs. Base-catalyzed copolymerization is preferred for higher molecular weight products. It depends on inherent copolymerization ratios; ie, the various cyclic siloxanes do not react at the same rates because of electronic and steric effects.

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Phenyl-substituted siloxanes are more reactive than methylsiloxanes. Ring strain explains the much greater reactivity of cyclic trimers over cyclic tetramers, eg. D_3 is more than one hundred times as reactive as D_4 (14). Methyl and phenyl tetramers require special care because of immiscibility effects. The phenyl tetramer polymerizes first and impedes the polymerization of the methylsiloxane (214). Typically, copolymers with up to 50 mol % phenylsilicone can be prepared without difficulty. Copolymer fluids and gums containing methylphenyl- and methylvinylsiloxane units are also prepared in this manner. Final equilibrated products have a random distribution of siloxane units (12,14,17).

Another technique is to polymerize a single cyclic siloxane that contains the desired substituents, such as a mixed methylphenyl, eg,

((CH₃)₂SiO)₂[(C₆H₅)₂SiO)₂

a mixed ethylmethyl, or a mixed methylvinyl cyclic trimer or tetramer. This method is limited by the effects of substituents on specific reaction centers; in other words the ease with which an Si—O bond is attacked and opened in the initiation step depends on the electronegativity and steric requirements of the substituents present on a particular silicon atom. Electron-withdrawing groups, eg, phenyl and trifluoropropyl, facilitate nucleophilic attack at silicon (14,213).

Because of the reactivity of the Si—H bonds, polymethylhydrogensiloxane homopolymers and random copolymers can only be prepared by acid equilibration at low temperatures. Polymethylalkylsiloxanes are usually manufactured by hydrosilation reactions, where the desired olefin adds Si—H provided by the acid-equilibrated polymethylhydrogensiloxane (67).

A third method of copolymerization gives block copolymers, such as silicone blocks of different compositions or silicone heteropolymers; specific catalysts are required. An example is the formation of block copolymers by the reaction of linear polydimethylsiloxanes with silanol end groups with p-bis(dimethylhydroxysilyl)benzene (a disilphenylenediol), using quaternary ammonium salt catalysts such as the n-hexylamine, or the tetramethylguanidine salts of di-2-ethylhexanoic acid (215).

High molecular weight copolymers of tetramethyl-p-silphenylenesiloxane and dimethylsiloxane have also been made by nonequilibrating, base-catalyzed polymerization (216,217):

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henylenesiloxane ;, base-catalyzed Vol. 15

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Polymers with varying dimethylsiloxane content can be made by varying the proportion of D₃.

Homopolymers of methyltrifluoropropylsiloxanes are also prepared by non-equilibrating, ring-opening reactions because the equilibrium mixture of the base-catalyzed reaction gives only a small amount of polymer. Copolymers with methyltrifluoropropylsiloxanes also require special techniques (218). Methyl-3,3,3-trifluoro-n-propylsiloxane trimer, [CH₃(CF₃CH₂CH₂)SiO]₃, reacts rapidly in the presence of NaOH at 150°C to give the linear polymer, which depolymerizes under these conditions to the cyclic tetramer. At equilibrium the product consists of 96 wt % cyclic and 4 wt % linear components (219). For high polymer the reaction of the trimer must be stopped at the proper time. Certain catalysts, eg, the sodium derivative of sodium acetate, NaCH₂COONa, facilitate this operation (220).

Reactivity Ratios. The base-catalyzed copolymerization of cyclic polysilox-anes can be analyzed in terms of the classical Mayo-Lewis reactivity ratio concept. This brings the effects of ring strain, steric requirements, and electronegativity of substituents clearly into focus. A series of polymerizable cyclic compounds showed an intrinsic reactivity difference of 160-fold between D_3 and the more reactive 2,2,5,5-tetraphenyl-2,5-disiloxacyclopentane,

with a ring-strain energy of ca 42 kJ/mol (10 kcal/mol). Mayo-Lewis-type reactivity ratios for several cyclic siloxanes have been determined. The reactivity of dimethyl trimer was 25-fold less than that of diphenyl trimer (221).

Silicone-Organic Copolymers. Silicone-organic block copolymers have been made with a variety of organic components. Both copolymerization and grafting prepolymerized segments together are employed. Block copolymers of silicones and organic polymers can provide physical strength as well as the durability and surface properties of silicones. Some compositions are compatible with organic plastics and are used as additives to improve processibility (222). Others have unique properties for special applications. Silicone-polyethers are used as surfactants with polyurethane foam, for example (12,67,213,223).

Siloxanes containing silanols or alkoxysilanes react with the hydroxy groups of organic polymers to give silicon-oxygen-carbon links between the polymers, as illustrated by the formation of silicone alkyds (224). The same type of reaction can be used for polyester, epoxy, phenol-formaldehyde, and acrylic compositions. The preparation of silicone-polyethers also utilizes the Si-O-C linkage (225). This linkage offers a potential (hydrolytically) weak point, but in practice the

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polymers are stable. The Si—O—C link can be avoided. For example, carboxyalkyl-functional or hydroxyalkyl-functional silicones can be used to make such copolymers by esterification or transesterification (226,227). Polyethers have been attached to siloxanes by linkages such as

$$\equiv$$
SiCH₂O(CH₂CH₂O),R

using the Williamson synthesis (228) or by adding Si—H to olefinic functional polyether chains to make linkages such as (229).

Silicone-polyimides are made by the reaction of ethanolamine derivatives of siloxanes with polyacids, such as 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid), or from aminoalkylsilicones, as shown below (179-181).

$$-O(CH_3)_2Si(CH_2)_nNH_2$$
 \xrightarrow{HOOC} \xrightarrow{COOH} polyimide-silicone where $n=2$ or 3

Dianhydrides can also be used with aminoalkylsilicones. A new kind of silicone-polyimide employs a dianhydride containing aryl-ether linkages. These copolymers have excellent mechanical, thermal, electrical, and processing properties; flammability is low, and combustion is accompanied by low acid gas generation (230,231).

Silicone-polycarbonates can be prepared by the reaction of phosgene with siloxane prepolymers terminated by free phenolic OH groups from bisphenol A, 2,2-bis(4-hydroxyphenyl)propane (232,233), after reaction with Si—Cl.

$$2 \longrightarrow SiO(C_6H_4)C(CH_3)_2(C_6H_4)OH + COCl_2 \longrightarrow 2 HCl + \{-SiO(C_6H_4)C(CH_3)_2(C_6H_4)O\}_2C, \text{ etc}$$

Procedures involving phase-transfer catalysis in the synthesis of these copolymers have been reported (234). By varying the size of the polysiloxane block and the ratio of silicone to 2,2-bis(4-hydroxyphenyl)propane, polymers ranging from elastomeric to hard resins can be synthesized. The effect of silicone content on the tensile and elongation properties of silicone—polycarbonate block copolymers is shown in Figure 7 (235,236).

The reaction of dipotassiopolystyrene with [(CH₃)₂SiO]₄ produces a silicone-polystyrene block copolymer (237,238). Other organic components of copolymers with silicone include acrylonitrile, isoprene, methyl methacrylate, nylon-6, urethane and 2-vinylpyridine (223).

Other types of copolymers have metal atoms in the siloxane chain. Reactions of titanium esters with silanols give titanoxysiloxane copolymers (239).

$$-(CH_3)_2SiOH + C_2H_5OTi$$
 \longrightarrow $-(CH_3)_2SiOTi$ $+ C_2H_5OH$

A large number of such metallosiloxane copolymers containing aluminum, tin titanium, boron, phosphorus, iron, and other elements have been made (240).







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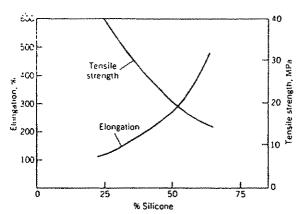


Fig. 7. The effect of silicone content on the tensile and elongation properties of silicone-polycarbonate block copolymers (236). To convert MPa to psi, multiply by 145.

They exhibit improved strength, but hydrolytic instability. However, species of this kind are probably involved when salts and esters of these metals function as silanol condensation catalysts.

Silicone-carborane copolymers with in-chain or pendent carboranyl groups have been synthesized. The former type can be made by the following reaction (241):

$$\begin{split} &(CH_{3}O)(CH_{3})_{2}Si-CB_{10}H_{10}C-Si(CH_{3})_{2}(OCH_{3}) + (CH_{3})_{2}SiCl_{2} \xrightarrow{FeCl_{1}} \\ &- \{(CH_{3})_{2}SiO(CH_{3})_{2}Si-CB_{10}H_{10}C-Si(CH_{3})_{2}O\} + 2 \ CH_{3}Cl_{2}Cl$$

Vinyl groups attached to pendent carboranyl groups can be readily introduced to provide cure points.

Copolymers in which the silicon is present to modify properties or provide room-temperature cure for organic polymer systems can be made with almost any organic polymer. Several such compounds have been reported, for example, with polyolefins (242), polyurethane (243), and polyether (244). Polysulfide polymers terminated by reaction with 3-glycidoxypropyltrimethoxysilane or 3-methacryloxypropyltrimethoxysilane have the following end groups:

These polymers offer a method of making copolymers with each other or with reactive silicones as the other component (245).

Properties

The best-known silicones are the trimethylsiloxy-terminated polydimethylsiloxanes. These polymers, as well as variations with silanol, vinyl, or hydride end groups, form the building blocks of many silicone fluid-based products and of most cured silicone elastomers. The properties of polydimethylsiloxanes are

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modified by substitution of methyl groups on the silicon atom by hydrogen, alkyl, phenyl, or organofunctional groups.

Silicones with viscosities ranging from <1 to 106 mm²/s (= cSt) are used directly or formulated into greases, emulsions, dispersions, sealants, and other silicone products. The unique physical, electrical, thermal, surface or surfactant, solubility, toxicological, and chemical properties of methylsilicones and the easy modification of these properties by incorporation of other organic radicals into the polymer have led to diversified applications in the food, cosmetic, medical, automotive, aerospace, electrical, electronic, construction, and other industries.

Linear polydimethylsiloxanes have been extensively studied. Because of weak intermolecular forces, the polymers have low melting points and second-order transition temperatures. For dimethylsilicone gums (rubber polymers) these are -50 and -85°C, respectively. They do not crystallize under ordinary conditions. The low intermolecular forces result in low boiling points for the lower molecular weight oligomers, low activation energy for viscous flow, high compressibility, small change of viscosity with temperature, and for resins and unreinforced elastomers, poor physical properties despite high molecular weights. Structural interpretation of many properties includes the high flexibility of siloxane chains; factors influencing the spatial extension of polysiloxane molecules are now better understood (12,14,18,246,247).

Volatile oligomers in the products of equilibration of MM and D_4 , eg, MD_rM and D_n , can be separated and purified by fractional distillation. Their properties show the effects of molecular size and structure in these systems (Table 5) and in related oligomers, such as M_4Q and TM_3 (67).

Table 5. Properties of MD,M and D,"

MDT formula	Melting point, °C	Boiling point, °C	Density d ²⁰ , g/cm ³	Refractive index. não	Viscosity (η) at 25°C, mm²/s	Flash point °C
MM	-67	99.5	0.7636	1.3774	0.65	-9
MDM	- 80	153	0.8200	1.3840	1.04	37
MD₂M	-76	194	0.8536	1.3895	1.53	70
MD ₂ M MD ₂ M	~ 80	229	0.8755	1.3925	2.06	94
MD₄M MD₄M	- 59	245	0.8910	1.3948	2.63	118
MD _a M	~78	270	0.9012	1.3965	3.24	133
-	- 63	290	0.9099	1.3970	3.88	144
MD ₆ M MD ₇ M	00	307.5	0.9180	1.3980	4.58	159
D ₃	64.5	134	1.125			
	17.5	175.8	0.9561	1.3968	2.30	69
D,	- 44	210	0.9593	1.3982	3.87	
D _s	-3	245	0.9672	1.4015	6.62	
D ₆	- 32	154°	0.9730	1.4040	9.57	
D ₇ D ₈	31.5	290	1.1770°	1.4060	13.23	

[°] Ref. 10.

In higher linear dimethylsilicone polymers, the number-average molecular weight is related to the bulk viscosity:

log (viscosity in mm²/s at 25°C) = 1.00 + 0.0123 $\overline{M}_n^{0.5}$ where $\overline{M}_n > 2500$

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b Crystals.

^c At 2.7 kPa (20 mm Hg).

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The intrinsic viscosity $\{\eta\}$ in dL g, determined by the extrapolation of the viscosity to zero concentration, has the following values (248.249):

 $[\eta] = 2 \times 10^{-4} \overline{M}_n^{0.66} \text{ (toluene)}$ and $[\eta] = 8 \times 10^{-4} \overline{M}_n^{0.5} \text{ (methyl ethyl ketone)}$

Branched polymers, made by introducing T or Q units, have lower bulk or intrinsic viscosities than linear polymers of the same average molecular weight. Even slight branching causes a noticeable decrease in the bulk viscosity (250).

The physical properties of several oligomers with various substituents are shown in Table 6. Many such oligomeric compounds have been prepared and described, and several are used as intermediates in the preparation of polymers (20,251,252).

Table 6. Properties of Siloxane Oligomers*

Compound	Boiling point, °C _{kPa} *	Density d ²⁰ , g/cm ³	Refractive index, n_0^{20}	Melting point, °C
[(C ₆ H ₆) ₂ SiO] ₆	3350.13	1.23°		200
[(CH ₂)(C ₆ H ₂)SiO],	2370.13-0.67	1.183	1.5461	99
(CH ₃) ₃ SiOSi(C ₆ H ₅) ₂ OSi(CH ₃) ₃	17224	0.984	1.4927	
[(CF ₃ CH ₂ CH ₂)(CH ₃)SiO],	1340.4	1.255	1.3724	
(CH2=CH)(CH3)SiO)	1111,3	0.9875	1.4342	- 43.5
(CH ₃) ₃ Si[OSiH(CH ₃)] ₂ OSi(CH ₃) ₃	177	0.8559	1.3854	
[(CH _a)(H)SiO),	134	0.9912	1.3870	- 69

º Refs. 20, 251, 252.

The unique flexibility of the siloxane chain and the fact that there is essentially no energy barrier for rotation around the siloxane bond result in low glass-transition temperatures, small changes in physical properties (except viscosity) with molecular weight, and small changes (compared with other polymer systems) with temperature. The viscosity of linear polydimethylsiloxanes is controlled by the incorporation of chain-terminating groups. Figure 8 shows the effect of molecular weight on the viscosity of polydimethyldisiloxanes (253). At molecular weights greater than 30,000 ($\eta=1000~{\rm mm^2/s}$ at 25°C), chain entanglement becomes a factor, as seen in a change in slope of the viscosity—molecular weight relationship. Although the data used to develop the relationship in Figure 8 were based on trimethylsiloxy-terminated polymer, the plot is also valid for other end groups. Polar end groups, silanol for example, change the slope, particularly at the lower molecular weights, where hydrogen bonding becomes a factor, leading to higher viscosities for equivalent molecular weights (253).

The polydimethylsiloxanes have Newtonian flow below 1000 mm²/s, but become more and more non-Newtonian as the molecular weight increases. This can be seen in Figure 9, where the effect of shear rate on viscosity is shown. The polymers are stable to shear stress, however, and return to their original viscosity after being stressed (10,14).

The effect of temperature on the viscosity of a polysiloxane is much smaller than for other organic polymers (254,255). Figure 10 shows the differences between two polydimethylsiloxanes (50 and 1000 mm²/s at 25°C) and two hydrocarbon fluids (with viscosities of about 15 and 300 mm²/s at 25°C) (10). The effect

^b To convert kPa to mm Hg, multiply by 7.5.

^c Crystals.

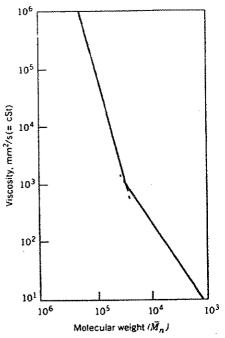


Fig. 8. The effect of molecular weight on the viscosity of linear methylsilicones (253).

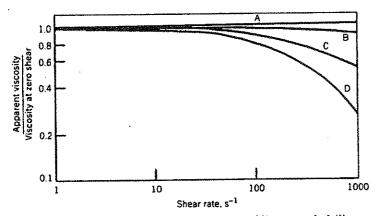


Fig. 9. The effect of shear rate on the viscosity of linear methylsilicones (10). A, 1,000 mm²/s; B, 5,000 mm²/s; C, 30,000 mm²/s; D, 100,000 mm²/s.

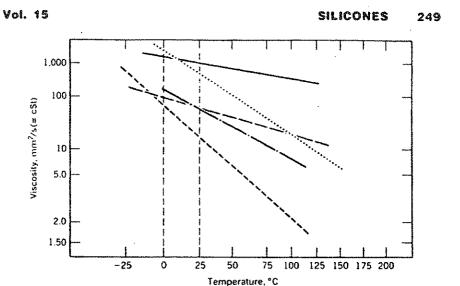


Fig. 10. Viscosity-temperature curves (10,256). —, 1000-mm²/s dimethylsilicone; —, 50-mm²/s dimethylsilicone; —, methylalkyl (C₁₀) silicone; …, 300-mm²/s hydrocarbon (mineral oil); …, 15-mm²/s hydrocarbon (mineral oil).

of replacing one methyl group on the silicon atom with a C_{10} hydrocarbon can also be seen (256). The viscosity change with temperature is greater than for the polydimethylsiloxane, but less than for the hydrocarbons (mineral oil).

The compressibility of polysiloxanes is unusually high (257,258). Figure 11 shows the compressibility of a cross-linked polymer used in mechanical shock absorbers (259), where this "liquid-spring" property of silicones is important. The cured polymer has almost 12% compression at 207 MPa (30,000 psi). A 50-mm²/s fluid also has a compressibility of about 12%; lower viscosity fluids (0.65–10 mm²/s) are somewhat more compressible (about 15%) at the same pressure. By comparison the compressibilities of mineral oils and water at 207 MPa (30,000 psi) are about 8 and 7%, respectively. Polysiloxanes containing phenyl or alkyl groups are less compressible than polydimethylsiloxanes, but more than hydrocarbons.

The surface properties of polydimethylsiloxanes are the basis for their applications as antifoam agents, foam stabilizers, internal lubricants, and external release or slip agents. The foam-stabilizing properties of the silicone-polyether copolymers further extend the use of these materials (235). Figure 12 compares the surface tension change with molecular weight of polydimethylsiloxane and polyisobutylene, a carbon analogue of the siloxane. The low surface tensions and mild impact of molecular weight are characteristic of the silicones. The interfacial tension against water is ca 42 mN/m (= dyn/cm); such fluids repel water when spread on glass (260).

Polydimethylsiloxanes are insoluble in water, about 30 ppb for the trimethylsiloxy-terminated polymer (261). Solubility in water increases when polar groups, including silanols, are incorporated into the polymer. The same polymer absorbs

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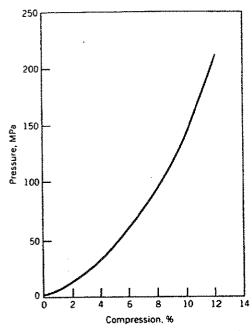


Fig. 11. Compressibility of a cross-linked methylsilicone polymer used in mechanical shock absorbers (259). To convert MPa to psi, multiply by 145.

about 300 ppm of water at high (95%) relative humidity (262). The solubility of water increases as the polarity of the silicones increases, and silicone-polyethers can be synthesized that are completely miscible with water (235).

Silicones have high gas solubility compared with other liquids and polymers. At 25°C and 101 kPa (1 atm), the air, nitrogen, and carbon dioxide solubilities are 0.17, 0.17, and 1.0 cm³/cm³, respectively (4). The solubility of oxygen in a 26,000-mm²/s fluid at 101 kPa is 0.2 mg/g, and that of hydrogen in D₄ is 0.07 mg/g (263). The high gas solubility results in high gas permeability; silicone rubber has carbon dioxide and nitrogen permeabilities about 1000 times those of polyethylene (264). This is an important factor in silicone membranes.

Silicones have excellent electrical properties and are widely used as fluids, resins, elastomers, and dielectric compounds in electrical and electronic insulation applications (263,265–267). These properties are affected by moisture and in the case of elastomers and dielectric compounds, by compounding ingredients and cure conditions.

Chemical Properties. The silicon-carbon bond and the siloxane bond have substantial thermal stability. Tetramethylsilane can be heated in the absence of air to 680°C before decomposition occurs (268,269). Various cyclic Si—C compounds are formed at 750°C (270), and complete decomposition occurs above 2000°C (271). The Si—C bond in methylsilicones ruptures in the absence of air in the 450-500°C range (19).

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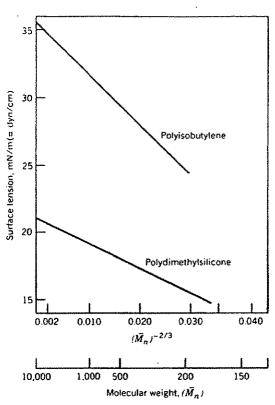


Fig. 12. The effect of molecular weight on the surface tension of polydimethylsilicone and polyisobutylene at 25°C (260).

The siloxane bond is less thermally stable than the silicon-carbon bond. Some silicone products are not affected up to 200-300°C (272,273). Measurable decomposition to cyclic oligomers starts at ca 320°C. This decomposition is accelerated by acid or base and is a reversal of the polymerization of cyclic compounds.

The silicon-carbon bond is vulnerable to oxidation near 200°C. Methylsilicones under some oxidative conditions give formaldehyde; more complete combustion gives carbon dioxide and water. Where oxygen ruptures an Si—C bond, an Si—O bond remains. At higher temperatures phenylsilicones form phenol (4.5.10.67).

In the absence of catalysts the hydrolytic depolymerization of silicones is very slow. They are attacked by steam and depolymerize when heated with water in a closed vessel (10,67). Unsubstituted alkyl groups resist cleavage, but methane is liberated when methylsilicones are heated with aqueous caustic at 200°C. Aryl groups are more susceptible to cleavage by both nucleophilic and electrophilic reagents (19). Overall, however, silicones are generally considered chemically resistant and durable in most environments.

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Polysiloxane Cures

The three curing (cross-linking) processes for polysiloxanes of commercial importance include condensation cure, peroxide-induced free-radical cure, and silane-olefin addition cure. Radiation cure with uv light is receiving a great deal of attention, and some commercial products cured with this technology are available. Electron beam, gamma ray, and plasma polymerization cure technologies have been investigated.

Condensation Cure. Solvent-borne silicone resins, reactive (silanol) fluids, and most RTV elastomers cure (cross-link) by condensation processes. A simple silanol condensation gives water as by-product.

Other common reactions include

$$\implies$$
SiOCH₃ + HOSi \implies \implies \implies SiOSi \implies + CH₃OH
 \implies SiH + HOSi \implies \implies \implies SiOSi \implies + H₂
 \implies SiOOCCH₃ + HOSi \implies \implies \implies SiOSi \implies + CH₃COOH
 \implies SiONR₂ + HOSi \implies \implies \implies SiOSi \implies + R₂NOH
 \implies SiNR₂ + HOSi \implies \implies \implies SiOSi \implies + R₂NH

A variety of catalysts initiate and accelerate condensation cure. Amines, including aminopropylsilane derivatives, and carboxylic acid salts of lead, tin, and zinc are commonly employed. Organic salts of iron, cadmium, barium, antimony, zirconium, and cadmium have been investigated. Tin(II) octoates, laurates, and oleates, as well as the salts of dibutyl tin, are particularly useful. The key requirement, besides catalytic activity, is solubility of the catalyst in the silicone polymer matrix. Strong acids (Brønsted and Lewis types) and bases effect condensation, but the reaction is difficult to control (67).

At low temperatures cure cycles require many hours or days; high catalyst concentrations and high (oven) temperatures (>150°C) shorten cure times. High catalyst concentrations can be a problem in some solventless systems, such as coatings. Rapid gelation, even at room temperature, may accompany catalyst addition in the absence of a solvent-dispersing medium. However, the condensation cure is used extensively in room- and elevated-temperature cure of solventless elastomer compositions where catalyst concentrations are not harmful.

Peroxide Cure. The most widely used process for curing or cross-linking high molecular weight polysiloxanes to elastomeric products employs small amounts of organic peroxides at elevated temperature (274). The most commonly used are the aroyl peroxides (dibenzoyl, bis-p-chlorobenzoyl, and bis-2,4-dichlorobenzoyl peroxides), alkaroyl peroxides (dicumyl), and the higher molecular weight derivatives of t-butyl peroxide (2,5-dimethyl-2,5-di-t-butylperoxyhexane). Optimum temperatures, other requirements, and cross-linking rates vary; chlorobiphenyls are formed from chlorobenzoyl peroxides (275).

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The action of the peroxides depends on the ability of free radicals arising from their decomposition at elevated temperatures to abstract hydrogen atoms from methyl groups. Ethylene links are thus formed between the siloxane chains (177):

These reactions were demonstrated when octamethylcyclotetrasiloxane heated with t-butyl perbenzoate gave bis(heptamethylcyclotetrasiloxanyl)ethane (276):

$$(CH_3)_2 \qquad (CH_3)_2 \\ Si \\ O \qquad O \qquad O \\ (CH_3)_2Si \qquad CH_3Si-CH_2-CH_2-SiCH_3 \quad Si(CH_3)_2 \\ O \qquad O \qquad O \\ Si \qquad O \qquad O \\ (CH_3)_2 \qquad (CH_3)_2 \qquad (CH_3)_2$$

The vinyl groups in polymethylvinylsiloxanes react vigorously with peroxides. They can easily be treated with weakly cross-linking peroxides such as those containing di-t-butyl peroxide groups.

$$\begin{array}{ccc} CH_3 & CH_3 \\ -Si - O - & RO & Si - O - \\ CH = CH_2 & CH - CH_2OR \end{array}$$

Hydrogen abstraction from a methyl group then leads to cross-linking.

All overall mechanisms would also include some radical propagation and termination steps. This mechanism accounts for the experimental observation that more than 1 mol of cross-links forms per mole of peroxide, but not per mole of vinyl groups. A polymer of low vinyl content (CH₂=CH/Si = 0.026) gave 2.4-3.2 cross-links per mole of peroxide and an average of 0.9 cross-links per mole of vinyl (276).

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Platinum-catalyzed Hydrosilation Cure. Metal-catalyzed cross-linking by hydrosilation has become increasingly important during the last decade (72,277-279). The term hydrosilation applies to the addition of Si—H across any unsaturated species.

The reaction has been extensively employed for the synthesis of organofunctional silanes and siloxanes (19,67,71). Cross-linking involves Si—H present in one polymer adding to vinyl groups in another polymer. Polymers containing multiple reactive sites give complex three-dimensional cross-linked structures. In contrast to condensation or peroxide cures, addition cures do not produce by-products.

Hydrosilation processes triggered by heat, light, radiation, and peroxides are free radical in nature and of limited use. Hydrosilation catalyzed by Group VIII precious metal complexes (platinum, rhodium, and ruthenium) is far more versatile and useful. The catalyst should be in a form soluble in the silicone system; platinum compounds are widely employed. These catalysts effectively promote addition cure at concentrations as low as 1–2 ppm. They are usually combined with a vinyl-functional silicone before mixing with a hydrogen-functional silicone for cure.

The precise mechanism of homogeneous hydrosilation catalysis has not been unequivocally established. It depends on the nature of the catalyst and of the molecular species undergoing reaction. Platinum—olefin complexes (278,279) are among the most efficient catalysts; a possible pathway for hydrosilation is depicted in Figure 13. The platinum metal atom is thought to be a site to which the Si—H and Si—CH=CH₂ can bond in the proper proximity and stereochemical configuration for addition to occur. For the catalyst to be effective, olefin ligands attached to the metal atom must be labile enough to permit substitution of vinyl groups attached to silicon and small enough to permit (oxidative) addition of Si—H without steric hindrance.

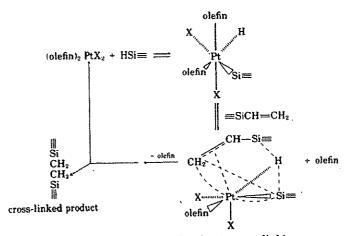


Fig. 13. Pathway for hydrosilation cross-linking.

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The catalyzed life of some silicone systems is too short for certain applications. In these cases inhibitors are included in the formulations to provide a sufficient pot life and temperature—cure profile, allowing operations like coating and molding to be carried out conveniently. An ideal silicone addition cure may combine instant cure at elevated temperatures with infinite pot life at ambient conditions. Commercial systems, however, always depart from this ideal situation, as depicted in Figure 14.

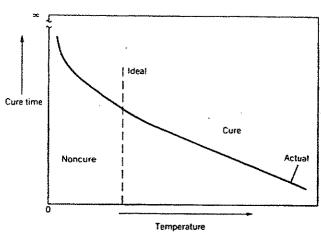


Fig. 14. Time-temperature relationships for inhibited hydrosilation-curing systems. The ideal case combines instant cure at a desired elevated temperature and infinite pot life at ambient temperature. In actual cases, as illustrated, the pot life is just extended below a practical threshold temperature.

A clue to the inhibitor function is provided by the cure mechanism described above (279). At some time during the process, both Si—H and Si—CH=CH2 groups must be coordinated with the platinum metal center. Any substance that prevents access to the catalyst at room temperature must not block coordination sites at cure temperature. An equilibrium is probably established between catalyst ligands, inhibitor molecules, and Si—H or Si—CH=CH2 groups about the metal atoms.

Figure 15 is a simplified representation of such an equilibrium. The inhibitor-metal complex is probably not a true compound, but rather resembles a solution where inhibitor molecules behave like a solvent. This would be consistent with the observation that effective cure inhibition requires large excesses (typically $10-10^2\,M$) of inhibitor molecules per catalyst atom. Increasing the inhibitor concentration lengthens pot life and slows cure in most cases, lending further support to the concept of an equilibrium among catalyst, inhibitor, and reactive silicone functions. The formation of the metal atom-inhibitor species is favored at room temperature, whereas the cross-linking reaction is promoted at elevated temperatures.

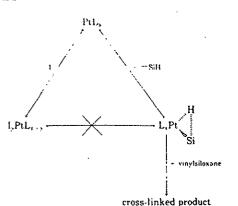


Fig. 15. Equilibrium for inhibited hydrosilation-curing systems; PtL_{\star} = catalyst, I = inhibitor, and L = catalyst ligand.

The inhibitors that provide useful pot life while permitting commercially useful cure rates include substances known to form compounds with the catalyst element. Classical complexing or chelating agents selected from nonmetals possessing unshared electron pairs, such as amines, phosphines, sulfur derivatives, and stannous compounds, are excellent inhibitors, but often form such stable compounds with platinum group metals that they act as poisons and prevent cure even at elevated temperatures. Unsaturated organic compounds such as olefins, acetylenes, and azo derivatives are much preferred. Platinum group metal complexes with numerous olefins are well characterized, and experiments have confirmed that olefin ligands are labile at elevated temperatures. Unsaturated substances are therefore unlikely to act as poisons. A wide variety of unsaturated organic compounds have found commercial use as inhibitors in solventless silicone compositions (280–283).

Hydrosilation is an exothermic process with a heat of reaction of ca 160 kJ/mol (38 kcal/mol). Differential scanning calorimetry is useful in product development work to optimize catalyst:inhibitor ratios for different application scenarios (279).

Uv Cure. Polymers combining silicone properties with ease of radiation processing have long been worthy of development. Most published work (mainly patent literature) has involved the syntheses of silicone polymers incorporating radiation-sensitive functional groups such as acrylates (284,285), oxiranes (286,287), or mercaptans (287). These methods have certain drawbacks limiting their use. Acrylated or methacrylated silicones require an inert atmosphere in the curing chamber for fast, complete uv cure. Epoxy-functional silicones can be uv cured in the presence of novel silicone-compatible onium salt photocatalysts (285). However, acid by-products limit their applications. Highly organofunctionalized silicones have properties less like silicones and more like those of standard organic plastics, when cured.

Free-radical-initiated hydrosilation is another technique. A photochemical route uses photosensitizers to generate radicals in the polymer system (288):

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The reaction proceeds slowly when the photosensitizers are only partially soluble in silicone. Certain photoactive peresters catalyze hydrosilation cure upon uv irradiation (289):

Even in an inert atmosphere, high concentrations of perbenzoate ester are required for rapid cure response.

High Energy Radiation Cure. Linear polydimethylsiloxanes can be crosslinked by irradiation with high energy radiation. High molecular weight linear polymers give a silicone rubber free of catalyst residues. Therefore, irradiated rubber has a much better heat resistance than peroxide-cured rubber (290,291).

Several energy sources are suitable, including radioactive cobalt, Van de Graaf generators, and resonance transformers (292). Irradiation leads to the formation of radicals (293,294):

$$\begin{array}{c|c} CH_3 & \rightarrow \dot{S}i-O \rightarrow \\ & \downarrow \\ CH_3 & CH_3 \\ & CH_2 \\ & \rightarrow \dot{S}i-O \rightarrow \\ & CH_2 \\ & \rightarrow \dot{S}i-O \rightarrow \\ & CH_3 \\ & CH_3 \\ & \downarrow \\ & CH_3 \\ & CH_$$

Chains can therefore be degraded or cross-linked, but cross-linking exceeds degradation, resulting in the formation of Si—Si, Si—CH₂—Si, and Si—CH₂—CH₂—Si links (295). Products isolated by distillation from the irradiation of octamethyl-cyclotetrasiloxane include bi(heptamethylcyclotetrasiloxanyl),

$$(CH_3)_2Si - O - Si - Si - O - Si(CH_3)_2$$

$$(CH_3)_2Si - O - Si - Si - O - Si(CH_3)_2$$

$$O O O O$$

$$(CH_2)_2Si - O - Si Si - O - Si(CH_3)_2$$

$$(CH_3)_2 (CH_3)_2$$

and bis(heptamethylcyclotetrasiloxanyl)methane.

$$(CH_3)_2Si - O - Si - CH_2 - Si - O - Si(CH_3)_2$$

$$O O O O O$$

$$(CH_3)_2Si - O - Si Si - O - Si(CH_3)_2$$

$$(CH_3)_2Si - O - Si (CH_3)_2$$

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Hydrogen, methane, ethane, and (probably) propane were detected as by-products of irradiation. Good agreement between the total gas yield and the polymerization yield is found between -40 and $+100^{\circ}\mathrm{C}$: yields increase with temperature and intensity of irradiation; divergence occurs above $100^{\circ}\mathrm{C}$ (295).

Radiation cure of a methylvinylsilicone rubber has been studied (296). The cross-linking process was random, with no differentiation between methyl and vinyl groups. Molecular weight development indicated that cross-linking and degradation occurred simultaneously. Other substituents on the Si atom alter the behavior of siloxanes toward irradiation. Phenyl groups increase irradiation resistance, whereas siloxanes containing Si—H bonds are highly sensitive (294).

Plasma-induced Cure. Plasma polymerization of low molecular weight siloxanes is used to form thin, hard silicone films on certain substrates (eg, polyimides) (297). Although of limited applicability, this technique offers a potentially valuable means to obtain insulating coatings on metallic and nonmetallic surfaces. The moisture barrier properties of plasma-polymerized hexamethyldisiloxane have been studied (298). Such coatings (thickness ca 5 μ m) provide substantial reductions in water permeation rates (298).

Plasma-polymerized silicone coatings are not homogeneous. An upper oligomeric layer covers the more dense and highly cross-linked main part. It is believed that oligomers primarily formed in cationic reactions are subsequently cross-linked by uv-initiated radical reactions, resulting in Si—CH₂CH₂—Si and Si—CH₂—Si linkages and some residual Si—H bonds. The cross-linking reactions are accompanied by reactions reducing organic content (299).

Silicone Fluids

A large number of silicone fluids have been synthesized and studied. Many are manufactured commercially, including dimethyl, methylalkyl, and dimethyl—diphenyl copolymers and silicone—polyether copolymers. Reactive fluids with silanol, alkoxy, or vinyl end groups share many properties with nonreactive fluids terminated with trimethylsiloxy groups. However, the reactive fluids are used in products where they are cured by appropriate methods.

Dimethylsilicone fluids and many reactive fluids are made by catalyzed equilibration of dimethylsilicone stock (hydrolysate or distilled cyclic compounds) with a source of chain terminator. With trimethylsiloxy, (CH₃)₃SiO_{0.5}, as chain terminator, this reaction produces mixtures of MD_xM and D_n polymers. The ratio of M to D in the charge controls the average molecular weight and the viscosity of the product. For example, a 50-mm²/s fluid has an average molecular weight of ca 3,000, a 350-mm²/s fluid ca 15,000, and a 1,000-mm²/s fluid ca 25,000. For low viscosity fluids the process can be run at about 180°C in a glass-lined reactor with acid clay catalysts or, at lower temperatures, with sulfuric acid; both batch and continuous processing are used (100).

Alkaline catalysts are used for the production of high viscosity fluids or gums. These polymers can be processed batchwise in kettles or continuously in a heated tube with stirring (175). Polymerization is continued in the case of gums to make polymers of over 500,000 average molecular weight and $10^7 \, \text{mm}^2/\text{s}$ viscosity. Some gums contain vinyl or phenyl substituents, which are introduced by



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copolymerizing $(CH_3)_2SiO$ with vinyl- or phenylsiloxanes. Phenyl substituents are added as $[(C_6H_5)_2SiO]_n$ or $[(CH_3)(C_6H_5)SiO]_n$, and vinyl substituents as $[(CH_3)(CH_2=CH)SiO]_n$, $[(CH_3)_2(CH_2=CH)SiO]_{0.5}$, or both.

In most instances the equilibrated fluid is devolatilized by heat and vacuum after catalyst deactivation. Both equilibration and devolatilization can be carried out in batch or continuous process systems. Fluids can be blended to fluids of intermediate viscosities. Since the properties of a polymer depend on molecular weight distribution and average molecular weight, blending can affect physical properties appreciably. Blends of fluids of widely different viscosities are less Newtonian in behavior than those with normal molecular weight distribution.

Properties. Properties of commercial silicone fluids are given in Table 7. Changes in pressure cause unusually large changes in volume and viscosity (257,258). The flow of dimethylsilicone fluids is Newtonian, meaning that the viscosity is constant over a broad range of shear rates for fluids of less than 1000 mm²/s, but the apparent viscosity decreases with the shear rate for higher viscosity fluids (300). The fluids are stable to shear stress, however, and return to original viscosity after being passed through small orifices under pressure. Thermal expansion of the volume is about 0.1%°C (4). The specific heat (1.4–1.6 J/g or 0.33–0.37 cal/g at 0–100°C) increases with viscosity (4).

The fluids spread over water and can form monomolecular films. When these films are compressed laterally, the ratio of stress to strain undergoes several changes associated with changes in the order and orientation of the molecules (302,303). The force required for compression is also a function of the pH. The interfacial tension against water is ca 42 mN/m. Spread on glass, the fluids repel water, forming a contact angle of about 103°, which is roughly the same as for paraffins.

Dimethylsilicone fluids are good hydrodynamic lubricants, but poor for sliding friction. For steel on steel the coefficient of friction is about 0.3-0.5. For some metal combinations, eg, brass on steel, the fluids are fairly good lubricants for medium or light loads (304).

Dimethylsilicone fluids are transparent to visible light and uv radiation of wavelengths above 280 nm; many strong selective bands occur in the ir region (see Analysis and Testing).

The velocity of sound at 30°C is 873.2 and 987.3 m/s for 65- and 1000-mm²/s fluids, respectively (305). It decreases with increased temperature and is significantly higher for methylphenylsilicones.

The dielectric constant (Table 7) decreases with temperature. For example, a 1000-mm²/s fluid has a dielectric constant of 2.76 at 30°C and 2.54 at 100°C (306). The power factor is low, but increases with temperature and behaves irregularly with frequency. Resistivity decreases with temperature. Gamma radiation reduces resistivity and dielectric strength (263). The latter is also affected by moisture (301).

Gases are soluble in dimethylsilicone fluids. The solubilities of air, nitrogen, and carbon dioxide are 0.17, 0.17, and 1.00 cm³/cm³ at 25°C and 101 kPa (1 atm), respectively (4). The solubility of oxygen in a 26,000-mm²/s fluid at 101 kPa is 0.2 mg/g, and that of hydrogen in D₄ is 0.07 mg/g (307). About 250-300 ppm water dissolves in silicone fluid at 25°C and 95% rh, whereas only 30 ppb of dimethylsilicone dissolves in water (261,262). The fluids are miscible with benzene, dimethyl ether, methyl ethyl ketone, carbon tetrachloride, or kerosene.

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• Refs. 4, 10, 67, 300, and 301.

• To convert W/(m·K) to (Blu·in.///h·ft².•F), divide by 0.1441.

• Approximate value.

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They are slightly soluble in acetone, dioxane, ethanol, and butanol and insoluble in methanol, ethylene glycol, and 2-ethoxyethanol (14).

Dimethylsilicones cross-link when subjected to gamma ray or electron radiation. Small radiation doses increase the viscosity with the formation of branching (308). Increased radiation dosages result in gelation. Polymerization has been observed in microwave discharges (309). Fluids containing $CH_3(C_6H_5)SiO$ or $(C_6H_5)_2SiO$ are more stable to radiation; methyl fluid is attacked 35 times more rapidly than phenyl fluid (310–312).

Oxidation of dimethylsilicones in an "oxygen lean" atmosphere yields formaldehyde and formic acid; complete oxidation gives silicon dioxide, carbon dioxide, and water. Each carbon-containing molecule formed represents a carbon cleaved from silicon and results in a siloxane linkage. Thus difunctional units are initially converted to trifunctional and then tetrafunctional units, and the polymer becomes branched or cross-linked. Eventually, all the silicone is converted to amorphous silica (10,313).

Prolonged heating of silicone fluids can result in devolatilization and cracking and therefore in loss of weight and change in viscosity. Heating under nitrogen at 300°C reduced the viscosity of a 100-mm²/s dimethylsilicone fluid by 47% in 480 h (17). Heating in air results in weight loss, and gelation occurs in about 200 h at 250°C. Stability is improved by antioxidants, eg, phenyl- α -naphthylamine, as well as by compounds of titanium, iron, and cerium (314,315). Ironcatalyzed preoxidation results in fluids that do not gel in 500 h at 315°C.

Replacement of the methyl groups by longer alkyl chains modifies the unique properties of dimethylsilicones. The activation energy for viscous flow $E_{\rm visc}$ and the rates of change of viscosity with temperature and pressure increase (14). Oxidative stability decreases, compatibility with organic compounds increases, and lubricity improves (256,316). At high temperatures diethylsilicone fluids are less stable than dimethyl fluids, but can be stabilized by chelate inhibitors, eg, copper ethyl acetoacetate (317). Methylalkylsilicone fluids are less stable than the dimethyl fluids. The methyl group confers unique stability; the longer alkyls are roughly equivalent in oxidation stability (256). Although ozone and electric corona discharge usually degrade organic polymers, they do not attack silicone fluids, gums, or derived elastomers with methyl or phenyl groups.

Phenyl substitution (methylphenyl or diphenyl) has some of the same effects as increasing the size of the alkyl group, but increases rather than decreases thermal or oxidative stability. Heat aging is further improved by phenyl substitution of the end groups (318). Copolymers of dimethylsiloxane with some methylphenylsiloxane have lower pour points (319) because the bulky groups interfere with crystallization of the methyl polymer; $E_{\rm visc}$ for MD'M, where D' = (C₆H₅)₂SiO, is 19 kJ (4.5 kcal) compared with 10 kJ (2.4 kcal) for MDM, indicating interference of the bulky phenyl groups with motion. Methylphenyl-silicone fluids with, for example, 8–50 wt % CH₃(C₆H₅)SiO, have lower flash points than dimethylsilicone fluids of the same viscosities; they are also less compressible.

Chlorinated phenyl groups, eg, tetrachlorophenylsiloxane copolymerized with dimethylsilicone fluids, increase lubricity (300), depending on the average number of chlorine atoms per phenyl group and the proportion of such groups in the copolymers (320).

Methyltrifluoropropyl silicone fluid changes viscosity rapidly with pressure

and therefore shows good lubricating properties (321) like methylalkyl fluids, where alkyl is octyl to tetradecyl. Methyltrifluoropropyl silicone has a solubility parameter of about 9.5 compared with about 7.5 for $(CH_3)_2SiO$ (322); it swells much less than $(CH_3)_2SiO$ in octane or toluene. 2-Cyanoethyl and 3-cyanopropyl substituents give copolymers with $(CH_3)_2SiO$ that may have solubility parameters of ca 9.0–9.5, ie, similar to that of fluorosilicone (254,323).

Vinyl groups provide reactive centers for peroxide and silane—olefin cures. They can be located along the chain for cross-links or may act as chain extenders when terminally located. In many higher molecular weight polymers vinyl concentrations are not high enough to affect physical properties (ie, <1%).

Incorporation of siloxane units with Si-H, particularly $CH_3(H)SiO$, affects the physical properties of fluids. Most important is the increase in chemical reactivity; water repellence remains good. The ability to cross-link readily increases the usefulness of silicon-hydride-containing polymers in textile and paper treatment and in hydrosilation curing of elastomers.

Polyethers have been introduced as substituents by various methods (49,225). The copolymers are water soluble and have higher viscosity-temperature coefficients and better load-carrying capacities as lubricants than (CH₃)₂SiO polymers. They are of practical interest because of their surfactant properties.

Other modified polymers have been prepared that include amino-, mercapto-, carboxy-, hydroxy-, glycidoxy-, and methacryloxyalkyl-substituted silicones. Such organofunctionality is usually incorporated to obtain specific physical and chemical properties. Aminoalkyl-substituted fluids, for example, increase water solubility. They are used in automobile polishes to enhance durability and confer detergent resistance through bonding with paint films. Other modified fluids perform as textile lubricants, softeners, and antistats and impart stain resistance. Organofunctional silicones can be used as additives to improve the processibility and performance of certain organic thermoplastics, thermoset resins, and elastomers. Reactive silicones provide numerous cure and copolymer possibilities. They can bond to various substrate materials to alter surface properties (67,173).

Production. The manufacture of silicone fluids requires a supply of various difunctional chlorosilanes purified by fractional distillation. In some cases the purification is difficult because of the presence of close-boiling coproducts of the reaction. For example, dimethyldichlorosilane is obtained routinely in high purity (~99.9%) using more than 100 plates in the distillation column to remove methyltrichlorosilane, which boils only 4°C lower. Less rigorous control of impurities results in undesirable variability in the viscosity characteristics in the finished fluids; specifically, trifunctionality leads to branching and departure from Newtonian behavior.

The simplest and most versatile hydrolysis procedure is the batch process, in which a mixture of chlorosilanes is added to water with agitation (184,185). The hydrolysis generates hydrogen chloride, which dissolves exothermically in excess water.

$$(CH_3)_2SiCl_2 + H_2O \longrightarrow [(CH_3)_2SiO]_n + HO[(CH_3)_2SiO]_mH + HCI$$

If only stoichiometric quantities of water are present, gaseous hydrogen chloride is evolved, and the overall reaction is endothermic. Acid acceptors, such as sodium

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bicarbonate, may be used to neutralize the hydrogen chloride and provide a neutral environment conducive to the formation and stabilization of terminal silanol groups. Concentrated hydrochloric acid facilitates the separation of the siloxane and aqueous phases since the specific gravity of the siloxane phase is close to that of water. Alternatively, hydrocarbon solvents may be added to the chlorosilane feed or to the hydrolysis vessel; in addition to lowering the density of the siloxane phase, the presence of solvents increases the proportion of cyclic oligomers formed during hydrolysis. Alcohol modifiers react with the chlorosilanes to form terminal alkoxy groups, which may be removed by subsequent hydrolysis. The same considerations apply also to hydrolysis of resins.

The proportions of various molecular species obtained in the hydrolysis depend on the reactants and on the conditions used, including the intensity of agitation; for example, the proportion of cyclic compounds formed in the hydrolysis of dimethyldichlorosilane is between 20 and 80% of the total, with the cyclic tetramer (D₄) predominating. The hydrolysate, after separation from the acid, is washed with water or a neutralizing bicarbonate solution, and dried by passing through an absorbent medium such as Fuller's earth. It is held for further processing, such as equilibration with chain-terminating groups.

Continuous processing is feasible for difunctional products produced in large volume, especially dimethylsiloxanes (324). In the processing scheme shown in Figure 16, hydrochloric acid is continuously circulated through a corrosion-resistant loop of piping, whereas dimethyldichlorosilane is metered in at one point. Upstream of the chlorosilane inlet, a portion of the circulating mixture is withdrawn into a settling chamber and separated into acid and siloxane phases. Centrifuges or hydrophilic-hydrophobic membrane systems improve separation. The siloxanes are neutralized by passing through carbonate solution and are stored for further processing. If the effluent hydrochloric acid is more concentrated than the azeotropic composition (21%), it can be distilled to yield gaseous hydrogen chloride, which can be dried and converted to trichlorosilane by reaction with silicon or used in the manufacture of methyl chloride, closing the chlorine cycle. Fresh makeup water, or the azeotropic solution resulting from hydrogen chloride stripping, is added to the hydrolysis loop to maintain the necessary proportion of reactants in the system. Small quantities of acid which are not recirculated may be allowed to settle to separate any residual siloxane; they are neutralized before discharge.

Because the media are strongly corrosive, equipment for the hydrolysis steps is typically made of glass, glass-lined steel, or chemical- and thermal-resistant plastic.

The second step in the preparation of finished fluids is an equilibration of triorganosiloxy units with linear and cyclic difunctional oligomers to produce chain-stopped linear molecules, which are stable against further rearrangement (325). The equilibration of M and D units produces a mixture of cyclic siloxanes and linear siloxanes with unreactive M units at the end of the chain; some cyclic siloxanes remain at equilibrium with the mixtures of linear molecules.

 $[(CH_3)_2SiO]_n \ + \ HO - \{(CH_3)_2SiO\}_m H \ + \ (CH_3)_3SiOSi(CH_3)_3 \ \frac{H - \ or \ OH - \ OH$

 $[(CH_3)_2SiO]_n \ + \ (CH_3)_3SiO - \{(CH_3)_2SiO\frac{1}{p_0}Si(CH_3)_3 \ + \ H_2O$

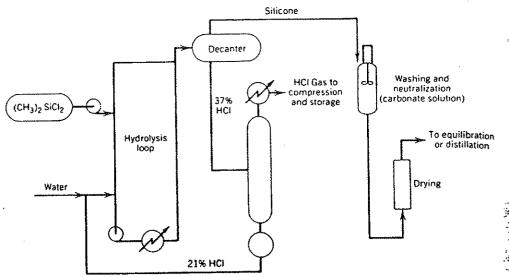


Fig. 16. Flow diagram for production of dimethylsilicone fluids.

The chain-terminating moieties are added in the form of disiloxanes prepared by separate hydrolysis of materials such as trimethylchlorosilane. The chain terminator may also be incorporated with the dichlorosilanes in the original hydrolysis. In either case the proportion of chain terminator is selected to yield the desired average molecular weight in the product. The mixture of siloxanes is treated in glass-lined or stainless steel equipment with a strongly acidic or basic catalyst at room temperature or up to 200°C for several hours. At the end of the equilibration, a statistically predictable distribution of molecular weights results, such as that shown in Figure 17. The fluid is washed with water to destroy the residual active groups (silanolates or silyl esters) and neutralized and dried by passing through an absorbent medium. The fluid may be devolatilized in batch vacuum stills, wiped-film evaporators, or molecular stills. This procedure yields a stable, neutral fluid of slightly higher viscosity than the original siloxane mixture, depending on the vigor of the stripping process. Empirical correction for chain-terminating groups lost during stripping is therefore necessary in determining the initial formulation (charge). Blending is sometimes helpful to achieve close viscosity control in the final product.

Derived Products. Several types of greases are made from mixtures of silicone fluids and fillers. For insulating and water-repellent greases, silica filler is used. The fluid may be dimethylsilicone alone or copolymerized with methylphenyl, methyltrifluoropropyl, or methylalkyl silicone. For lubricating grease the fillers are usually lithium soaps, and the preferred fluids are methylphenyl, chlorinated phenylmethyl, or methyltrifluoropropyl silicones. The electrical properties of silica-filled greases are good. Such dielectric compounds are workable at low temperatures and do not have a dropping point like soap-filled greases. Lubricating greases vary in properties, depending on the fluid and thickener. They

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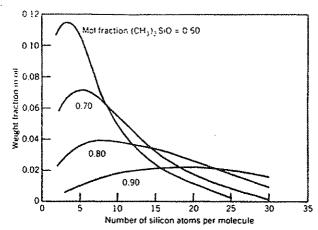


Fig. 17. Molecular distribution of linear dimethylsilicones after equilibration with chain terminator.

have wide service temperature ranges (-70 to 230° C); dropping points of $200-260^{\circ}$ C, depending on the soap; low bleed; and low evaporation rate and weight loss in a vacuum. Greases based on fluids with good lubricating properties are capable of prolonged performance up to 200° C (67).

Emulsions of silicone fluids in water are vehicles for applying small amounts of silicone to textiles, paper, and other surfaces. Concentrations are between 20 and 60 wt % silicone, except for foam-control agents, which may contain as little as 10 wt %; various emulsifiers are used. The emulsified silicone fluids may be of any type, but are usually dimethyl- or methylalkylsilicones. As antifoaming agents they disperse rapidly in aqueous systems, but for nonaqueous systems, eg, crude oil or vegetable oils, 100% silicone or a solvent solution of the silicone is used (67).

Silicone Resins

Silicone resins are highly cross-linked siloxane systems. The cross-linking components are introduced as trifunctional or tetrafunctional silanes in the first stage of manufacture. For example, a solution of CH_3SiCl_3 , $(CH_3)_2SiCl_2$, $C_6H_5SiCl_3$, and $(C_6H_5)_2SiCl_2$ or $CH_3(C_6H_5)SiCl_2$ in toluene is hydrolyzed to form a complex copolymer mixture, which remains in solution in toluene. The aqueous hydrochloric acid is separated, and the resin solution is washed and heated in the presence of a mild condensation catalyst to adapt (body) the resin to the proper viscosity and cure time. It is finally adjusted to specifications by distilling or adding solvents (4,10). The properties of the resins depend on the choice of chlorosilanes, the degree of cure, and the processing conditions.

Properties. The chlorosilanes for a particular resin formulation determine its characteristics. Monomethyl-, dimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, together with silicon tetra-

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chloride, have been most widely used. Prediction of specific resin properties as a function of composition frequently fails since processing and cure influence the final molecular configuration and related characteristics. However, some generalizations can be made: trifunctional siloxy units produce harder, less flexible resins, which are frequently immiscible with organic polymers; difunctional siloxy units increase softness and flexibility; and phenylsiloxanes are more miscible with organic polymers than methylsiloxanes and produce resins that are less brittle and have superior thermal resistance. Alkyl groups other than methyl also increase the compatibility with other organic materials. The effects of silanes on the properties of a film are shown in Table 8. Properties vary considerably; some resins are soft and flexible, and others are hard and glassy. This is depicted in Figure 18 in terms of the temperature dependence of Young's modulus (ie. stress for a unit elongation). Processing conditions vary from hydrolysis in strong acid to dilute acid or buffered aqueous systems; alkoxysilanes can also be used to avoid acid conditions. Solvent, temperature, concentration, and catalyst for bodying and curing affect the result.

Table 8. Effect of Silanes on the Properties of Silicone Resin Films*

Property	CH₃SiCl₃	C ₆ H ₅ SiCl ₃	(CH ₃) ₂ SiCl ₂	$(C_6H_5)_2SiCl_2$	CH ₃ (C ₆ H ₆)SiCl
hardness	increase	increase	decrease	decrease	decrease
brittleness	increase	great increase	decrease	decrease	decrease
stiffness	increase	increase	decrease	decrease	decrease
toughness cure speed	increase much faster	increase some increase	decrease slower	decrease much slower	decrease slower
tack	decrease	some decrease	increase	increase	increase

^a Ref. 10.

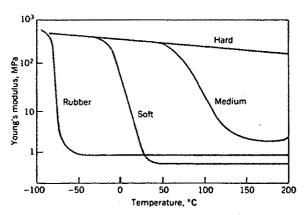


Fig. 18. Range of silicone resin properties in terms of the temperature dependence of Young's modulus (10). To convert MPa to psi, multiply by 145.

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Most silicone resin products require heat and catalysts for curing. During the life of the product, curing continues, and properties change with time. Latent-curing resin systems are based on quaternary ammonium salts (326).

Dipping or impregnating varnishes based on silicone resins are used to bond and insulate electrical coils and glass cloth; they are usually supplied as 50 or 60 wt % silicone resins in an organic solvent. Components are repeatedly dipped, drained, and baked to build up the required thickness. They are finally cured by a longer bake; time and temperature are determined by the resin used and the complexity of the component structure. The final bake usually lasts several hours at 204–260°C, although lower temperatures can be used (10).

Silicone laminating resins are used first to coat glass cloth; this coating is partially cured to a nontacky stage. Stacks of treated cloth are pressed at ca 7 MPa (1000 psi); high pressure laminates are heat cured. Vacuum forming or so-called bag molding takes place at lower pressures. Typical properties of a freshly cured impregnating resin are shown in Table 9 (17); laminate properties are shown in Table 10 (17,327).

Table 9. Properties of Silicone Impregnating Resins*

Property		Value	
heat endurance at 250°C, h			
flexure life*		250	
craze life ^c		750	
thermal life ^d , h			
at 300°C	•	500	
at 275℃		1500	
at 250°C		4500	
weight loss after 3 h at 250°C, %		4	
-	Dry		Wet
electric strength', V/μm	60		40
power factor at 25°C			
at 100 Hz	0.0084		0.0085
at 10 ⁶ Hz	0.0043		0.0047
dielectric constant at 25°C			
at 100 Hz	3.0		3.0
at 10 ⁶ Hz	2.9		2.9

[°] Ref. 17.

Pressure-sensitive adhesives are made by compounding silicone elastomer gums with silicone resins, which are not completely compatible with each other. They are available as solutions in volatile solvents and are applied to the backing by conventional knife-coating techniques. After the solvent is evaporated, a sticky film is left. It is cured by heating with a peroxide or other catalyst to develop strength and reduce tack. Fillers increase cohesive strength and reduce tack (328).

b Hours at which a film on a copper strip cracks when bent around a small rod.

[&]quot; Hours after which cracking is visible and evident without bending.

d Hours of aging to reduce electric strength of a glass cloth impregnated with silicone varnish to 50% of its initial value.

^{*} Electrodes 5 cm in diameter.

Table 10. Properties of Silicone-Glass Laminates*

Property	Value
tensile strength, MPa*	200-240
elongation at break, ?	1-2
flexural strength, MPab	140-310
compressive strength, MPab	140
modulus, MPa*	
flexure .	
at 25°C	$1.4 \times 10^4 - 2.4 \times 10^4$
at 260°C	$1.3 \times 10^4 - 1.7 \times 10^4$
tension	$1.0 \times 10^4 - 1.9 \times 10^4$
impact, Izod, J/m ^c	260-1300
distortion temperature, °C	>200
electric strength, V/µm	10-16
power factor, %	
at 103 Hz	0.5
at 10 ⁶ Hz	0.001-0.002
arc resistance, s	220-350

^a Refs. 17 and 327.

Water-repellent resins applied to masonry surfaces coat the pores and repel water. Hydrostatic pressure can overcome this surface activity. There is no continuous film to bar water or water vapor. Water-repellent resins are generally based on methyl or longer alkyl monomers. Release resins are baked on the metal surfaces of baking pans to prevent materials from sticking.

Paints are made from silicone resin solutions by mixing with stable inorganic pigments, such as titania, carbon black, or aluminum flakes. Silicone paints are very stable, and even after oxidation the residual polymer bonds the pigment. Silicone—aluminum paint is usable to 260°C. Silicone paints containing TiO₂ or other pigments are not discolored by heat or weathering. They have good gloss retention, hardness, mar resistance, flexibility, and resistance to soap, fat, and fruit juices.

Sodium methyl siliconate is made by dissolving CH₃SiO_{1.5} polymer in aqueous NaOH. This solution behaves like a solution of CH₃Si(OH)₂(ONa) monomer. On acidification the methylsilicone resin precipitates at a rate dependent on dilution and pH. Methyl siliconic acid, CH₃Si(OH)₃, is a weak acid; even carbon dioxide decomposes the sodium salt and leads to precipitation of the polymer.

Reinforcing fillers do not perform the same function in resins as in rubbers. Particulate reinforcing agents are not widely used because they do not increase tensile strength. They are used to fill and harden molding compounds and pressure-sensitive adhesives. Colloidal silica is used as a reinforcing coreactant in silicone resins, forming abrasion-resistant coatings on plastics (329,330). Incorporation of silylated uv absorbers improves the curability and protects the plastic against uv degradation (331).

Silicone resins are cured through the formation of siloxane linkages by the condensation of silanols. This is a continuation of the overall condensation process



C.A.

⁶ To convert MPa to psi, multiply by 145.

^{&#}x27;To convert J/m to (ft-lbf)/in., divide by 53.38 (ASTM D256).

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by which the resin is prepared. As condensation continues, the rate decreases because of lower silanol concentration, increased steric hindrance, and reduced mobility. For final cure, therefore, the reaction must be accelerated by heat and catalyst. Even so, some silanols remain, and slow cure continues for the life of the resin. The reaction is reversible, and water must be removed from the system to permit a high degree of cure (4,10). Many substances catalyze silanol condensation, including acids and bases (19); soluble organic salts of lead, cobalt, tin, iron, and other metals (332); and organotin compounds, eg, dibutyl tin dilaurate, or N,N,N',N'-tetramethylguanidine salts (333,334).

Silicone resins based on hydrosilation cure have also been developed. These materials cure by addition reactions and are similar in composition to hydrosilation-curing elastomers, albeit more highly cross-linked (335-337).

Silicone resins change little on exposure to humidity, heat, and sunlight. Weather resistance is also exhibited by silicone—organic copolymers and blends, provided the silicone content is high enough. A modified silicone varnish film shows a flexure life of 1000 h at 200°C and 150 h at 250°C and a craze life of 2000 h at 200°C and 800 h at 250°C (17). Its thermal life ranges from 35 h at 300°C to 2200 h at 225°C. Silicone-modified paints have excellent color and gloss retention on aging.

Production. The first step in preparing silicone resin consists of formulating an appropriate blend of organochlorosilanes. The blend may be mixed with inert solvents, which serve to modify the hydrolysis rate and provide a diluent for the hydrolyzed resin. The most widely used solvents are mineral spirits, esters such as butyl acetate, chlorinated hydrocarbons, toluene, and xylene.

Resin hydrolysis is complicated by a number of factors not encountered in processing silicone fluid. The hydrolysate tends to gel and become insoluble if the content of trifunctional or tetrafunctional chlorosilanes is too high, the solvent concentration is too low, or conditions are not carefully controlled to prevent excessive silanol condensation. Gel formation can be minimized by the addition of modifiers, usually low molecular weight alcohols, which react with chlorosilanes to yield alkoxysilanes rather than silanols. The former condense less easily and are converted to siloxanes during subsequent processing.

A second complicating factor is the difference in the hydrolysis rates of various chlorosilanes. In general, the rate of hydrolysis under given conditions increases with increasing functionality and decreases with increasing molecular weight of the organic substituent groups. Conditions must be balanced to promote the incorporation of all the hydrolysate products in the average resin molecule in order to obtain the desired final properties. This can be achieved through proper selection of solvent, intensive agitation, and sometimes, sequential addition of the chlorosilanes to be hydrolyzed.

The hydrolysis process for resins is not understood in detail. The products usually represent a statistical distribution of constituent groups and molecular weights. Tetrameric ring structures, as in fluid hydrolysates, are the most common intermediate configurations (95).

In practice, a considerable excess of water is used for hydrolysis, and the chlorosilane-solvent mixture is fed at a controlled rate. Evolved hydrogen chloride dissolves in the aqueous phase and is later separated. If a near-stoichiometric

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quantity of water is used, the order of addition may vary. The hydrogen chloride escapes as a gas and may be recovered in an absorption tower. In both cases the hydrolysate enters the solvent phase, but its average molecular weight and structure and the proportion of silanol groups generated for further condensation differ considerably with the hydrolysis conditions. Water input, feed rate, hydrolysis temperature, proportion and type of solvent, and intensity of agitation can affect the molecular structure of the hydrolysate and the properties of the finished resin. After hydrolysis the aqueous layer, if any, is withdrawn, and the resin is washed. When chlorinated solvents are used, the resin layer has a higher specific gravity than the aqueous layer and in batch equipment must be withdrawn and recycled. With other solvents it is frequently necessary to wash with a salt solution to separate the phases.

Resin hydrolysis may be carried out batchwise or continuously. The latter process has, in theory at least, the advantage of providing better uniformity since each increment of hydrolysate is processed in the same way; the molecular weight distribution should therefore be narrower. As in the case of batch hydrolysis of silicone fluids, the standard equipment for resins is a jacketed agitated kettle. Auxiliary equipment includes a feed tank and metering system. For continuous processing an agitated multistage contactor is employed, equipped with provision for the escape of hydrogen chloride gas. Glass-lined or other acid-resistant construction is required throughout.

Following hydrolysis, residual acid is removed by stripping out a small amount of solvent. The acid may also be left in to serve as a catalyst for further condensation of silanol groups, if this step is required. Partial condensation, or bodying, generates larger molecules with lower residual silanol content, allowing a rapid cure to a completely cross-linked resin after the solvent has been removed. After the resin hydrolysate has been washed and neutralized, special condensation catalysts, such as metal soaps or acid-treated clays, may be added to promote bodying. Some solvent may be stripped off to permit attaining the higher temperatures necessary for rapid condensation or to promote intermolecular silanol reactions. The end point is influenced by the concentration of resin solids in the solution; it is determined by viscosity measurement. At the completion of the bodying step, the temperature is reduced by quenching with additional solvent. After addition of curing catalyst, filtration, and blending to the desired final solvent content, the resin solutions are packaged in drums. For most bodying and finishing operations, stainless or carbon steel equipment may be used, provided the system is kept dry.

The processing of MQD resins is similar to that outlined above for DT resins, except that the separate hydrolysates are blended and equilibrated in a process similar to that described for the manufacture of silicone fluids. As an alternative to silicon tetrachloride as a starting tetrafunctional material, processes have been designed based on the conversion of sodium silicate to a silicic acid solution, which is treated with chlorosilanes (338).

Solventless resins in solid form are also offered for sale. They are made by careful removal of solvent at low temperatures in a vacuum drum dryer. These resins are compounded with glass flock or other fillers to produce silicone molding compounds.



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Silicone Elastomers

Cross-linking silicone polymers of appropriate molecular weight provides elastomeric properties. Fillers increase strength through reinforcement, and extending fillers and additives, eg, antioxidants, adhesion promoters, and pigments, provide specific properties (67,339,340).

Many curing (cross-linking) systems have been developed commercially for silicone elastomers. Different silicone elastomers are conveniently distinguished by their cure system chemistries and can be categorized by the temperature conditions needed for proper cure (341-343). Most compositions are based on polydimethylsiloxanes:

R is determined by the cure system chemistry. It can be hydrogen, an organic radical, or a silyl radical. The silyl radicals can contain single or multiple reactive groups like vinyl or alkoxy. Small amounts of reactive functionality are sometimes present in the chain in (copolymerized) units such as $(CH_2CH)(CH_3)SiO$. The value of x varies mainly with the type of product. For RTV products, x is in the 200–1,500 range; for heat-cured products x is ca 3,000–11,000.

Fillers. The reinforcing fillers for silicone elastomers are finely divided silicas made by fume or wet processes (344–348). The fume process provides the highest degree of reinforcement; the particle size must be small. The particle diameter should be about the length of a fully extended polymer chain, ie, 1 μ m, for semireinforcement and 0.01–0.05 μ m for strong reinforcement. Fine particle size does not necessarily provide good reinforcement because finely divided fillers tend to agglomerate and are hard to disperse. This tendency can be countered by treating the filler to give it an organic or a silicone coating before mixing it with polymer. Hexamethyldisilazane, [(CH₃)₃Si]₂NH, is sometimes used as a coupling agent (349). Treating the silica particles with hot vapors of low molecular weight cyclic siloxanes, ie, D₃, D₄, or D₅ (350), reduces agglomeration and prevents premature crepe hardening.

Nonreinforcing fillers, such as iron oxide or titanium dioxide, may stabilize or color the product or lower the cost per unit volume. Carbon black or carbon fibers provide electric conductivity (351).

Thus fillers of many different chemical compositions with a broad range of particle sizes and physical properties are suitable for silicone elastomers. The mechanism of reinforcement has not been unequivocally determined and may indeed vary from one filler or polymer type to another. However, particle size is of prime importance for the strength of the elastomer compound after cure. Effective reinforcement is provided by silica particles (sp gr ~2) with a range of 20–400 m²/g specific surface area.

Nonreinforcing fillers are sometimes used merely as extenders; particle size ranges from submicro-meter to about 10 μm . These fillers may not improve physical properties, but can be incorporated in significant amounts without adversely

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affecting strength. Manufacture of these extenders does not require the specialized technology necessary for extremely fine particle fillers, but they must meet rigorous requirements of thermal stability, electrical resistance, low volatile content, and chemical purity.

Silicone elastomers differ in several important ways from most organic elastomers. The most striking difference is the degree to which the strength of the final compound depends on the reinforcement conferred by the incorporation of fillers. Typical unfilled silicone gums, when cross-linked, are weak and soft, with tensile strengths on the order of 0.34 MPa (50 psi). Compounding with suitably reinforcing fillers may increase the tensile strength as much as 50-fold. The selection of the filler is therefore extremely important for applications where strength is required. Furthermore, because of the excellent thermal and electrical properties of the polymers, performance may in some cases be limited by the stability of the fillers rather than the polymer. These differences in polymer—filler interactions and physical property requirements make fillers suitable for silicone elastomers different from those used for natural and synthetic rubber compounding.

The preferred filler types for silicone compounds include finely divided silicas prepared by vapor-phase hydrolysis or oxidation of chlorosilanes, dehydrated silica gels, precipitated silicas, diatomaceous silicas, and finely ground high assay natural silicas; fumed titania, alumina, and zirconia have also been used. Pigment-grade oxides, especially ferric oxides, are extensively used as fillers for high temperature compounds in oxidizing environments. The iron oxide stabilizes the polymer against atmospheric oxidation and preserves the elastomeric characteristics, especially resilience and deformability, after exposure to temperatures above 300°C. Carbon blacks have had limited application because of their high content of adsorbed volatiles, which can lead to void formation during cure. Some blacks form conductive networks, which reduce the volume resistivity of the compound; they may be used when a controlled electrical resistivity lower than that of the parent polymer is desired. The conductivity can be increased with high concentrations of conductive fillers such as graphite and metal powders. Other types of fillers include calcium carbonate, clays, silicates, and aluminates. Fibrous fillers improve tear resistance at the expense of elongation, and hollow glass or plastic microspheres reduce the specific gravity. Fillers and their effects on heat-cured rubber properties are shown in Table 11.

Some silica or other oxide-filled silicone elastomers tend to "structure," ie, to form an elastic mass before cure, impeding normal processing operations such as molding and extrusion. Intensive working of the compound with a rubber mill or other mixer may be necessary to restore plasticity. To minimize this tendency, plasticizers and process aids are incorporated into the compounds; the most commonly used additives are monomeric or oligomeric organosilicon compounds (353). High surface silica filler is treated with a silicon derivative to minimize the buildup of structure. The structuring tendency is associated with hydrogen bonding between the siloxane polymers and silanol groups on the filler surface. The extent of hydrogen bonding is a function of the concentration of surface silanol and varies with the type and method of preparation of the filler. Surface silanol concentration can be related to the total surface area as determined by absorption methods. Sufficient treating agent can be added to react completely with or be hydrogen bonded to the silanol groups present and yield a nonstructuring rubber

